UNIVERSITAT ROVIRA I VIRGILI

IMPACTE RADIOLÒGIC AMBIENTAL CAUSAT PER LA INDUSTRIALITZACIÓ AL TRAM BAIX DEL RIU EBRE

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IMPACTE RADIOLÒGIC AMBIENTAL CAUSAT PER LA INDUSTRIALITZACIÓ AL TRAM BAIX DEL RIU EBRE

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TESI DOCTORAL
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Dr. Francesc Borrull i Dra. Carme Aguilar

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UNIVERSITAT ROVIRA I VIRGILI
Departament de Química Analítica
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El Dr. FRANCESC BORRULL BALLARÍN, Catedràtic del Departament de Química Analítica i Química Orgànica de la Facultat de Química de la Universitat Rovira i Virgili, i

La Dra. CARME AGUILAR ANGUERA, Professora Agregada del Departament de Química Analítica i Química Orgànica de la Facultat de Química de la Universitat Rovira i Virgili,

FEM CONSTAR:

Que la present Tesi Doctoral, que porta per títol: "IMPACTE RADIOLÒGIC AMBIENTAL CAUSAT PER LA INDUSTRIALITZACIÓ AL TRAM BAIX DEL RIU EBRE", presentada per ELENA FONOLLOSA GARCÍA per optar al grau de Doctor per la Universitat Rovira i Virgili, ha estat realitzada sota la nostra direcció, a l'Àrea de Química Analítica del Departament de Química Analítica i Química Orgànica d'aquesta universitat, i que tots els resultats presentats són fruit d'experiències realitzades per l'esmentada doctoranda.

Tarragona, 22 de juny de 2016.

Dr. Francesc Borrull Ballarín   Dra. Carme Aguilar Anguera

“El peligro de la radioactividad no reside en la emisión,

sino en su radio de acción.." (Lusnoc, 2011)

Un cop finalitzada aquesta aventura professional i personal tan enriquidora, es l'hora d'agrair a totes les persones que d'una manera o d'un altra han contribuït a fer d'aquest projecte una realitat.

En primer lloc, agrair als meus director de tesis, la Dra. Carme Aguilar i el Dr. Francesc Borrull, la confiança dipositada en mi per realitzar la tesi doctoral a la Unitat de Radioquímica Ambiental i Sanitària (URAIS), així com també a la Dra. Sandra Peñalver que encara que no sigui la tutora real, és la que ha estat més prop guiant-me cada dia.

També m'agradaria agrair totes les paraules de suport, motivació i recolzament del personal d'URAIS, sense ells la tesi no hagués estat possible. Primer, al Dr. Antonio Nieto, que tot i que van ser pocs els mesos compartits, vas ser capaç de que trobés un enfoc i la motivació necessària per començar aquest projecte. Agrair també a l'analista, Alícia Pla, per tota l'ajuda en la realització d'algunes de les analítiques. Finalment, a l'última incorporació al laboratori, Joana Martínez, ha sigut breu la nostra estada juntes però des del primer moment hem compaginat molt bé i hem pogut aprendre molt l'una de l'altra.

També fer menció al cap del laboratori del Consorci d'Aigües de Tarragona (CAT), Agustí Colom, i al cap de producció, Josep Ruana, per tots els consells i suport a l'hora de fer mostrejos sigui on sigui (vam arribar fins i tot a Escatrón!). També voldria agrair a tot el personal del laboratori del CAT que en un moment o en un altre m'han donat ajuda i consells a través de la seva experiència, Jordi, Aldea, Roser, Josepa, Anna i Amaya. Així com també a la última incorporació, Miquel, que tot i que hem coincidit poc temps, ha estat suficient per fer excursions, cafès i xerrades (i com jo et dic sempre: "qui et marejarà quan jo marxi?"). També voldria fer una menció especial a la meva companya de quilòmetres, per tots els consells, paraules de suport i ànims, i com no també totes les mostres que m'ha passat pel "seu" ICP.

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Per acabar, moltíssimes gràcies Jordi, per tot el suport durant aquest difícil camí, per la comprensió, il·lusió, suport i també pels moments de desconnexió de la feina.

ÍNDEX

Capítol 1

INTRODUCCIÓ

En el camp de la radioactivitat, cada cop s'està estudiant més l'impacte radiològic ocupacional i ambiental produït per les activitats realitzades per indústries convencionals no nuclears [1–5]. Aquestes es caracteritzen per utilitzar en els seus processos de producció matèries primeres que contenen radionúclids naturals o bé, per produir productes comercials, subproductes o residus enriquits amb aquests radionúclids. Són les conegudes com indústries NORM, acrònim de *Naturally Occurring Radioactive Material*. En aquests estudis s'ha determinat principalment la concentració d'activitat de la matèria primera, i dels productes i sub-productes generats, en els que s'ha pogut veure un increment de la radioactivitat. A més a més en aquests estudis, s'ha realitzat una quantificació de diferents radionúclids de manera individual, tals com ^{226}Ra, $^{238, 234}$U, $^{232, 230}$Th, ^{210}Po i ^{210}Pb, per estudiar-ne els possibles efectes sobre la salut, utilitzant els principis bàsics de la toxicologia. Els resultats d'aquestes publicacions ressalten la importància de fer estudis de monitorització de radionúclids d'origen natural en aquest tipus d'indústries i en el seu entorn.

A part de les indústries esmentades anteriorment, també hi ha altres que generen residus amb radionúclids artificials, aquestes són les instal·lacions nuclears. Entre tots els radionúclids produïts en les detonacions nuclears, els que tenen una major importància dosimètrica a l'atmosfera són els emissors beta (^{90}Sr, ^{137}Cs) i els emissors alfa (^{238}Pu, ^{239}Pu i ^{240}Pu), degut al llarg període de semidesintegració i a la radiotoxicitat que presenten.

Les principals vies d'eliminació de residus d'aquestes indústries, tant si són indústries NORM com instal·lacions nuclears, són mitjançant els efluents emesos a l'atmosfera (efluents gasosos), els efluents emesos al medi aquàtic (efluents líquids) i finalment els efluents sòlids els quals són emmagatzemats, tractats o eliminats més fàcilment [6]. Per tant, aquests residus poden afectar radiològicament a l'entorn, tant des del punt de vista mediambiental com toxicològic (espècies que viuen en aquesta zona).

Aquesta tesi doctoral, realitzada al laboratori de la Unitat de Radioquímica Ambiental i Sanitària (URAIS) i coordinada pel Grup de Cromatografia i Aplicacions Mediambientals de la Universitat Rovira i Virgili (URV), és una continuïtat de la línia de treball establerta amb les dues primeres tesis doctorals, realitzades per la Dra. Marta Palomo i la Dra. Montserrat Mola [7,8], centrades en l'àmbit de la radioactivitat ambiental.

En la primera tesi doctoral realitzada per la doctora Marta Palomo, es va iniciar la línia de recerca centrada en aquest àmbit a la Universitat Rovira i Virgili. Així doncs, en aquesta tesi es van posar a punt mètodes per determinar els nivells de radioactivitat (tant natural com artificial) en mostres ambientals de diferents orígens. A més, amb el desenvolupament d'aquests mètodes es va poder avaluar la radioactivitat ambiental d'alguns punts del riu Ebre. En la segona tesi doctoral es va continuar amb la temàtica establerta, i en aquest sentit es van desenvolupar nous mètodes analítics (alguns automatitzats) per a la determinació de diversos radionúclids individuals, tenint en compte la problemàtica de les indústries NORM.

Seguint amb la temàtica establerta per les dues tesis anteriors, en la present tesi doctoral s'ha realitzat un estudi radiològic sobre l'impacte que poden tenir algunes de les indústries presents a la conca del riu Ebre en l'entorn. Per això, s'ha fet una quantificació de diferents isòtops (naturals i artificials) en mostres ambientals en zones on hi pot haver una influència industrial. D'altra banda, també s'ha estudiat la possible afectació/bioacumulació dels diferents radionúclids d'origen natural en organismes aquàtics que es produeixen i consumeixen a la zona (delta de l'Ebre). Finalment, en l'última part d'aquesta tesi doctoral s'ha fet una estimació de la dosi efectiva degut a la ingesta d'aliments, tals com els mol·luscs produïts al delta de l'Ebre.

1.1. El riu Ebre

El riu Ebre està situat al nord-est de la península Ibèrica sent el riu més cabalós que desemboca a la Mediterrània. Té una longitud aproximada de 928 Km i una conca hidrogràfica de 85.362 km^2, dels quals, més de 84000 km^2 pertanyen al territori espanyol i la resta a França i Andorra [9].

L'Ebre neix a Peña Labra (a 1.980 m d'altura), desemboca i ressorgeix a Fontibre (Cantàbria). Després de recollir l'aigua de diferents serralades (Cantàbrica, Pirineus i Sistema Ibèric), entra als Països Catalans per Mequinensa on rep el cabal del Segre-Cinca i més avall del riu Siurana. Finalment, desemboca al mar Mediterrani, a prop de les poblacions de Deltebre i Sant Jaume d'Enveja, formant un ample delta en una zona sedimentària d'aproximadament 320 Km^2.

El riu Ebre és un riu regulat pels embassaments de Mequinensa i Riba-roja. Aquests embassaments produeixen actualment que el Delta pateixi un fenomen de regressió, ja que aturen els sediments que haurien d'arribar a la desembocadura [10].

Aquest estudi, principalment se centra en el tram baix del riu Ebre (últims 130 quilòmetres aproximadament), des de la comarca de la Ribera d'Ebre, passant per les comarques del Baix Ebre i Montsià fins a la desembocadura. A la Figura 1.1 podem veure una ampliació de l'últim tram del riu amb les diferents indústries que hi ha presents i que seran d'interès en el nostre estudi, tals com la indústria de fosfat bicàlcic situada a Flix, la central nuclear (CN) d'Ascó i finalment l'estació de tractament d'aigua potable (ETAP) situada a l'Ampolla. En aquesta figura també podem veure que al delta de l'Ebre es troben les badies del Fangar i els Alfacs, d'interès en la tesi donat que en aquestes badies es produeixen grans quantitats de mol·luscs tant per al consum de la zona com per a la comercialització externa.

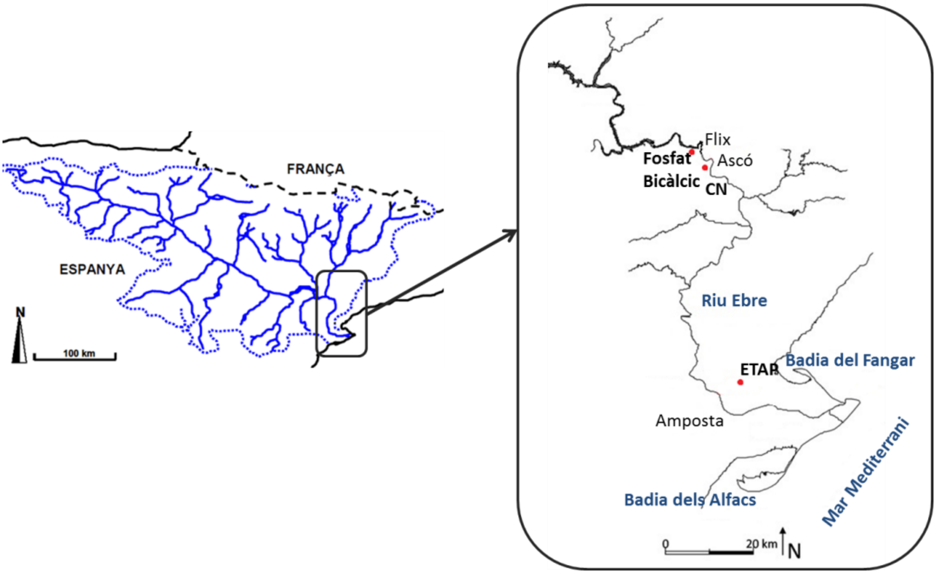


Figura 1.1 Esquema de la conca hidrogràfica de l'Ebre i detall de l'últim tram del riu (des de la comarca de la Ribera d'Ebre fins a la desembocadura).

En aquesta tesi doctoral, s'ha considerat adient la realització d'una descripció de les indústries que operen al tram baix del riu Ebre i que poden afectar a la qualitat tant de l'aigua com de les espècies que viuen en aquesta aigua. Així doncs, seguidament es farà una revisió bibliogràfica de les principals indústries que tenim presents en la part baixa del riu, i dels nivells de radioactivitat que s'han trobat en diferents estudis ja realitzats anteriorment.

A més a més, donat que les aigües de les badies (Alfacs i Fangar) són riques en nutrients, i alimenten la gran concentració d'algues planctòniques que són la base de la cadena tròfica dels mol·luscs que es produeixen, s'ha realitzat una síntesi bibliogràfica per veure la capacitat que poden tenir aquests mol·luscs de bioacumular diferents radionúclids.

1.2. Industrialització a la conca del riu Ebre

Actualment, hi ha un gran consum antropogènic de l'aigua del riu Ebre pel que fa a diversos sectors. A la Figura 1.2 es reflecteix el percentatge d'ús d'aigua del riu Ebre [9]. Cal destacar que a la conca de l'Ebre hi ha un notable desenvolupament hidroelèctric, tant pel nombre de salts hidroelèctrics, 457, com per la potència instal·lada, 3894,5 MW. L'ús hidroelèctric ve a ser d'uns 38000 hm^3/any d'aigua. Concretament, el sistema dels embassaments del Baix Ebre: Mequinensa-Ribarroja-Flix acull les tres centrals més productives de la conca.

D'altra banda, les centrals nuclears també tenen una elevada demanda d'aigua dolça per a la refrigeració, concretament l'única central nuclear activa a la conca de l'Ebre és la central nuclear d'Ascó. Aquesta central presenta dues unitats iguals, i cadascuna d'elles, té un sistema nuclear de producció de vapor format per un reactor d'aigua lliure a pressió (PWR). La demanda hídrica d'aigua dolça és de 2.270 hm^3/any.

També s'utilitza l'aigua per a la refrigeració de l'única central tèrmica de carbó en operació, la d'Andorra (Teruel) amb una demanda de 18 hm^3/any. En canvi, les centrals de gas de cicle combinat presents també a la conca (Arrúbal, Castejón, Escatrón i Castellnou) tenen una demanda hídrica menor.

Altres usos industrials amb demandes hídriques baixes, comprenen el sector metal·lúrgic, alimentari, d'aqüicultura, indústria manufacturera, etc.

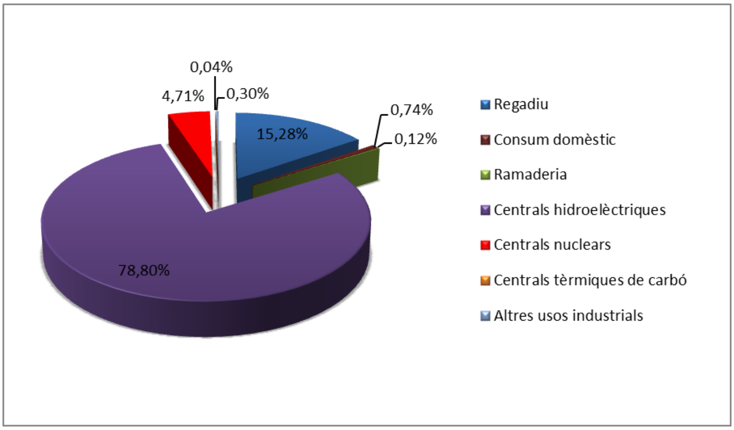


Figura 1.2. Ús de l'aigua del riu Ebre en els principals sectors [9].

Podem destacar que la comarca de la Ribera d'Ebre té la major demanda hídrica, donat que l'aigua del riu s'utilitza en nombrosos usos industrials. Al municipi de Flix, hi ha la indústria Ercros (dedicada a la producció de fosfat bicàlcic) instal·lada a la part dreta de l'embassament. Seguint el curs del riu, també al marge dret, concretament a la població d'Ascó, hi ha instal·lada la central nuclear.

Seguidament es farà una descripció de les indústries que poden incrementar la presència de radionúclids tant naturals com artificials al medi ambient degut al seu funcionament. D'una banda, tenim les centrals nuclears que augmenten exclusivament els nivells de radionúclids artificials. I d'altra banda, es presentarà una breu descripció de les indústries *Naturally Occurring Radioactive Materials* (NORM) que augmenten els nivells de radionúclids naturals a través dels seus processos. Després, es particularitzarà amb les indústries NORM que tenim presents al tram baix del riu Ebre.

1.2.1. Centrals nuclears

Les centrals nuclears generen durant el seu funcionament normal residus radioactius. Els residus d'alta i mitjana d'activitat són emmagatzemats a la mateixa central per a ser tractats convenientment, en canvi els de baixa activitat, després d'aplicar els criteris de seguretat marcats, són abocats com a efluents gasosos i líquids al medi ambient [11].

Com s'ha comentat anteriorment, l'única central nuclear activa a la conca del riu Ebre és la d'Ascó, concretament al marge dret del riu Ebre, al meandre que es forma entre les poblacions de Flix i Ascó. Aquesta central nuclear consta de dues unitats iguals amb un sistema nuclear de producció de vapor format per un reactor d'aigua a pressió i tres circuits de refrigeració. D'una banda utilitza l'aigua del riu Ebre per a refrigerar els condensadors, i d'altra banda, aboca els efluents líquids de baixa activitat al riu.

El Consell de Seguretat Nuclear (CSN) du a terme un programa amb la finalitat d'avaluar i vigilar l'impacte radiològic ambiental de les instal·lacions nuclears i radioactives. La vigilància radiològica del medi ambient es realitza mitjançant un sistema de xarxes, constituït per una xarxa de vigilància a l'entorn de les instal·lacions i per una xarxa nacional. Cadascuna de les instal·lacions s'encarrega del seu Programa de Vigilància Radiològica Ambiental (PVRA) seguint les directrius del CSN, en funció del tipus d'instal·lació i de les característiques de la zona, tals com la demografia, usos de la terra i l'aigua i hàbits de la població [12].

D'acord amb el programa de vigilància radiològica ambiental, les activitats dels efluents radioactius líquids de la central nuclear d'Ascó es mostren a la taula següent (Taula 1.1) [12].

Taula 1.1. Activitat dels efluents radioactius líquids (Bq/any). Any 2014. (ND = no detectat).

	Ascó I	**Ascó II**
Ag-110m	$3{,}09 \cdot 10^{8}$	$1{,}23 \cdot 10^{8}$
Co-58	$7{,}98 \cdot 10^{8}$	$7{,}32 \cdot 10^{8}$
Co-60	$7{,}24 \cdot 10^{8}$	$1{,}28 \cdot 10^{9}$
Cs-134	$3{,}99 \cdot 10^{8}$	$1{,}95 \cdot 10^{7}$
Cs-137	$5{,}57 \cdot 10^{8}$	$1{,}03 \cdot 10^{8}$
H-3	$2{,}53 \cdot 10^{13}$	$3{,}20 \cdot 10^{13}$
I-131	$2{,}93 \cdot 10^{7}$	ND
Mn-54	$3{,}73 \cdot 10^{7}$	$4{,}15 \cdot 10^{7}$
Sr-90	$3{,}54 \cdot 10^{8}$	$4{,}47 \cdot 10^{7}$
Altres	$2{,}07 \cdot 10^{9}$	$1{,}55 \cdot 10^{9}$

Al llarg de la història, s'han realitzat diferents estudis per a veure l'impacte radiològic degut als abocaments controlats d'aquesta instal·lació en les aigües del riu Ebre [13,14]. En els diferents estudis s'ha pogut observar que aquests abocaments produeixen l'augment de l'activitat de radionúclids artificials en les aigües del riu, tals com la presència d'isòtops d'estronci i triti (analitzats mitjançant detectors d'escintil·lació líquida). A més, en un dels estudis es va suggerir la possibilitat d'utilitzar el triti com a radiomarcador de l'aigua del riu per determinar el coeficient de dispersió longitudinal i la velocitat de les aigües del riu. Els resultats d'aquest estudi mostren la dispersió dels contaminants solubles al riu Ebre (aigües avall de la CN), aquesta informació podrà ser útil per a establir mesures d'emergència en cas d'abocament accidental d'aquests contaminants [15,16].

Més recentment, en el nostre grup de recerca es va fer un estudi on es va avaluar l'impacte de les indústries presents en el tram baix del riu Ebre mitjançat mostres de sediments, aigua superficial i mostres de biota (concretament en dues espècies d'algues) de 2002 fins a 2009 [17]. En les mostres d'aigua es va determinar l'activitat alfa total, beta total, triti, i isòtops emissors gamma. En canvi, en les mostres sòlides i biota es van determinar exclusivament isòtops emissors gamma mitjançant un detector de germani. Els resultats obtinguts en les mostres d'aigua superficial del riu Ebre mostren concentracions d'activitat de triti mitjanes de 2 a 50 Bq/L durant el període estudiat. Aquests valors són atribuïts a la presència de la CN, donat que d'altres rius sense presència de CN com el riu Ter i el riu Llobregat presenten activitats inferiors al límit de detecció (2 Bq/L) en aquest paràmetre. En canvi, les mostres de sediments procedents de l'àrea del delta de l'Ebre i del mar just a la desembocadura del riu, no mostren valors significatius de radionúclids artificials. A més a més, en el nostre grup de recerca s'ha fet un altre estudi per a la determinació selectiva d'alguns isòtops, com és el cas del ^{90}Sr [18]. Aquest estudi se centra en la separació selectiva de ^{90}Sr i ^{210}Pb mitjançant un mètode automatitzat en una instal·lació NORM situada a uns quilòmetres aigües avall de la CN d'Ascó. Les activitats obtingudes durant els 4 mesos d'estudi (març, juny, setembre i desembre) van ser de 34 a 76 Bq/kg (pes sec).

A nivell internacional, hi ha altres estudis centrats en l'impacte de CN. Concretament, aquests es basen en la determinació de radionúclids artificials en mostres sòlides i d'aigua en zones influenciades per CN [19,20]. Un dels isòtops més estudiats mediambientalment són els de cesi [21]. Aquests isòtops són emissors de raigs gamma i normalment són analitzats per mesura directa d'espectrometria gamma utilitzant detectors de germani. Un exemple és l'estudi de Eyrolle i col. [19] on van determinar les concentracions d'activitat de radionúclids antropogènics (^{137}Cs, ^{60}Co, ^{54}Mn, ^{11m}Ag, ^{238}Pu, $^{239+240}$Pu) en sediments de diferents localitats de França properes a la conca del riu Rhône, donat que hi ha instal·lats diversos reactors nuclears al llarg del riu. Les concentracions dels diferents radionúclids mostren una tendència decreixent amb l'augment de la descàrrega, els quals reflecteixen els nivells de fons geoquímic o antropogènic d'aquest sistema fluvial.

Uns altres radionúclids d'alt interès tant en els efluents líquids com sòlids de les CN són el ^{55}Fe i ^{63}Ni, degut a les reaccions d'activació que tenen lloc en els reactors nuclears [22]. El ^{55}Fe és un emissor beta de baixa energia amb una vida mitjana de 2.7 anys. Normalment es troba present en els residus radioactius, la seva presència pot ser atribuïda al fet que el ferro és un dels principals constituents dels materials utilitzats en centrals nuclears amb reactors d'aigua pressuritzada [22]. El ^{63}Ni és un emissor beta pur amb una vida mitja de 98.7 anys i aquest és majoritàriament produït als reactors nuclears com a producte d'activació (resultat de les reaccions del ^{62}Ni i ^{63}Cu). L'interès de separar aquests dos isòtops es deu a que tots dos són emissors beta de baixa energia i emeten en els mateixos intervals d'energia. Aquests dos isòtops han estat estudiats a la bibliografia en diferents mostres d'aigua procedents dels efluents de les CN [23,24]. A més, aquests radionúclids també han estat determinats en diferents mostres ambientals com sòl, peix, sediments, molsa, etc. [25,26].

Per tal de separar aquests dos isòtops hi ha diferents estratègies, tot i això la més utilitzada inclou els processos següents: una digestió de la mostra (en cas que sigui una mostra sòlida), separació dels radionúclids mitjançant reïnes específiques i finalment detecció mitjançant un detector d'escintil·lació líquida [24–28].

Finalment, cal destacar que en l'actualitat la majoria dels estudis de la bibliografia estan basats en la determinació de la radioactivitat que hi ha al medi ambient després de l'accident nuclear de Fukushima (ANF) que va ocórrer a Japó (2011)[29–33]. En aquestes publicacions s'ha pogut veure que més del 80% del material radioactiu de l'ANF va ser dipositat als oceans. En els diferents estudis es determina l'activitat d'isòtops artificials en sediments en zones de la costa per tal d'estimar la influència de l'ANF. Per exemple, en l'estudi de Nagaoka i col. [30] es determinen els nivells de ^{134}Cs i ^{137}Cs (3.8 – 206.7 Bq/kg i 6.1 – 296 Bq/kg, respectivament), de ^{90}Sr (ND – 0.26Bq/kg) i de ^{239,240}Pu (0.17 – 0.78 Bq/kg) en 51 mostres de sediments marins de la costa d'Ibaraki (Japó). Amb aquests resultats, els autors conclouen que tant l'activitat de ^{137}Cs com la de ^{90}Sr va augmentar després l'accident, en canvi, l'activitat dels isòtops de Pu es va mantenir igual. El mateix comportament dels isòtops de Pu es va veure en l'estudi de Oikawa i col. [32], on es determina l'activitat de diferents isòtops de Pu en sediments (a diferents profunditats) de diferents illes japoneses. Tot i obtenir un valor mitjà de $^{239+240}$Pu de 1.3 ± 1.2 Bq/ kg, no es va veure una contribució important d'activitat de Pu procedent de l'ANF.

1.2.2. Indústries NORM

El terme 'indústries NORM', de l'anglès *Naturally Occurring Radioactive Material*, es refereix a tota activitat minera o industrial que tingui el potencial d'augmentar la concentració de radionúclids d'origen natural continguts al medi mitjançant els seus processos [34]. Aquestes indústries preconcentren els radionúclids naturals, tals com ^{40}K i els isòtops procedents de les cadenes de l'^{238}U, ^{235}U i ^{232}Th, conegudes com sèries d'urani, actini i tori, respectivament (Figura 1.3) [35].

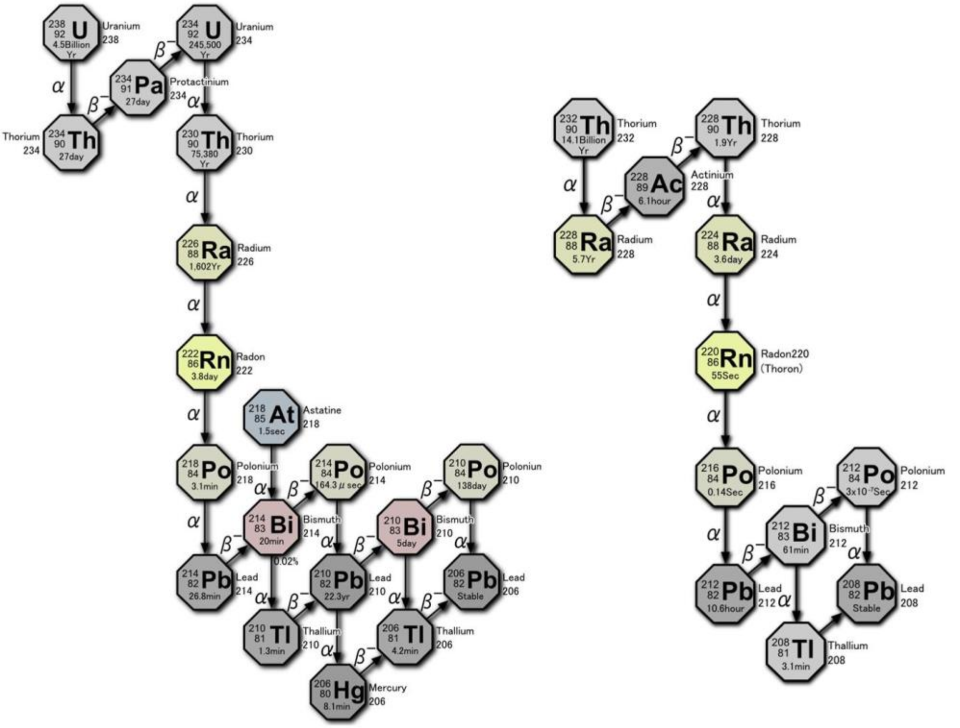


Figura 1.3 Sèrie de decaïment de l’urani-238 i tori-232 [35].

Els sectors industrials que estan dintre de la indústria NORM han estat identificats per la IAEA [36] i lleugerament modificats a la versió final de la nova directiva europea BSS (B*asic Safety Standards*) [37]. A continuació exposarem els diferents sectors industrials NORM, en ordre descendent de prioritat, per ser els més propensos a requerir regulació:

Extracció d’elements de terres rares

Els elements de terres rares s’utilitzen en l’electrònica, la il·luminació, la fabricació de imans, superconductors i ceràmica, catalitzadors químics, etc. S’extrauen mitjançant processos químics a partir de la monazita, la bastnasita, la xenotima i argiles que continguin terres rares. Aquests minerals contenen nivells de concentracions d’activitat de ^{232}Th entre pocs becquerels per gram fins a diversos centenars. En canvi, els residus i els efluents líquids i gasos dels processos d’extracció, contenen ^{232}Th i/o ^{226}Ra en concentracions d’activitat significativament superiors als de les matèries primeres utilitzades. Així doncs, l’eliminació i el tractament d’aquests residus, així com la descàrrega dels efluents líquids que contenen altes concentracions d'activitat de ^{228}Ra, han de ser gestionats sota un control regulador.

Producció i ús de tori i dels seus compostos

El concentrat de tori s'obté de processar la monazita i altres minerals rics en tori. Els materials implicats en els processos de producció tendeixen a tenir altes concentracions d'activitat de tori (o ^{228}Ra), les quals poden donar lloc a riscos de radiació, pel que s'han d'adoptar mesures de protecció radiològica. A més a més, l'exposició al toró també pot ser un perill significatiu, particularment en espais confinats, com per exemple dipòsits d'emmagatzematge.

Producció de niobi i ferro-niobi

La producció de niobi requereix processos químics d'alta temperatura, en canvi la producció de ferro-niobi es du a terme mitjançant una reacció exotèrmica també d'alta temperatura entre el piroclor i la pols d'alumini. L'escòria, tant en el cas de la producció de niobi com de ferro-niobi conté normalment al voltant d'uns 100 Bq/g de ^{232}Th. A més, l'ús d'altes temperatures genera pols que conté ^{210}Pb i ^{210}Po a concentracions d'activitat entre 100 i 500 Bq/g.

Extracció de minerals diferents a l'urani

Encara que les concentracions d'activitat dels radionúclids d'origen natural en la majoria de les roques no superen significativament el contingut d'un sòl estàndard, en ambients tancats (mines) s'acumula gran quantitat de radó a l'aire (fins 1000 Bq/m^3). La concentració de radó està influenciada principalment per diversos factors relacionats amb l'entrada del radó a l'aire, l'eliminació de radó de l'aire i el grau d'equilibri entre el radó i els seus descendents.

Producció de petroli i gas

L'aigua continguda en les formacions de petroli i gas conté diferents isòtops dissolts (^{228}Ra, ^{226}Ra i ^{224}Ra) juntament amb els seus descendents, procedents de la roca del jaciment. Quan aquesta aigua es porta a la superfície, amb el petroli i el gas, els canvis de temperatura i pressió poden conduir a la precipitació del radi (sulfats i carbonats de radi) a les parets internes dels equips de producció, així com també als llots i tancs del procés de producció. Les concentracions d'activitat de radionúclids en aquest procés són molt complicades de predir (van de nivells insignificants fins a més de 1000 Bq/g).

Producció de pigments de diòxid de titani

Les principals matèries primeres per a la producció de diòxids de titani són la ilmenita ($TiO_2 \cdot FeO$) i el rútil (TiO_2). Tant la ilmenita com el rútil presenten activitats de les sèries de decaïment de l’^{238}U i el ^{232}Th inferiors a 2 Bq/g i s’obtenen de les sorres amb minerals pesants que contenen monazita, zirconi, granat i xenotima. El pigment de diòxid de titani és pràcticament lliure de radionúclids naturals que contenia el mineral ja que tota la radioactivitat d’aquest mineral apareix en les aigües dels efluents i residus sòlids. Així doncs, només es troben altes concentracions d’activitat de radionúclids en les incrustacions, concretament ^{228}Ra i ^{226}Ra (<1 a 1600 Bq/g). Per tant, només es requereix atenció reguladora en els casos d’exposició de treballadors.

Indústria de fosfats

Les roques de fosfats presenten baix contingut de radionúclids (generalment menor de 3 Bq/g) i s’utilitzen com a matèries primeres per a la producció d’àcid fosfòric, fertilitzants i altres productes que contenen fòsfor. La producció d’àcid fosfòric genera grans quantitats de fosfoguix que conté radi a concentracions d’activitat similars a la de la roca original. D’altra banda, es formen incrustacions que contenen radi a l’interior dels equips utilitzats en el procés, en aquest cas, les activitats són 1000 cops més elevades que les de la roca original.

Indústries de zircó i zircònia (òxid de zirconi).

El zircó normalment s’obté de les sorres que contenen minerals pesats, aquestes contenen una activitat d’^{238}U entre 2 i 4 Bq/g. Pel que fa a l’elaboració de l’òxid de zircòni, el principal problema associat és que requereix altes temperatures per fondre la sorra de zircó. La major part del ^{210}Pb i ^{210}Po del material es converteix en fum de sílice, que es retira mitjançant un sistema de recollida de vapors. Per tant, l’exposició dels treballadors a aquests vapors de sílice ha d’estar controlat ja que aquestes partícules suspeses contenen fins a 200 Bq/g de ^{210}Pb i fins a 600 Bq/g de ^{210}Po.

Producció d’estany, coure, alumini, zinc, plom, ferro i acer

Encara que les concentracions d’activitat de radionúclids en les matèries primeres no són més elevades que els nivells ambientals normals, les altes temperatures utilitzades en els processos de fusió i refinació poden donar lloc a concentracions d’activitat de ^{210}Pb i/o ^{210}Po en la pols del precipitador de fins a 200 Bq/g. A més, els radionúclids es concentren en les escòries (entre 1 i 10 Bq/g).

Combustió de carbó

La combustió del carbó per produir calor i electricitat genera cendres volants i cendres de fons pesat o escòria. Les concentracions d’activitat de radionúclids en la cendra tendeixen a ser significativament més elevades que en el carbó, generalment són superiors a 1 Bq/g. Els radionúclids més volàtils com són el ^{210}Pb i ^{210}Po poden ser acumulats a les cendres volants i a les superfícies internes del bollidor-cremador on es troben concentracions d'activitat de ^{210}Pb en les incrustacions formades de més de 100 Bq/g.

Tractament d'aigües

El tractament d'aigua es practica a gran escala per eliminar els contaminants. Aquests processos sovint eliminen els radionúclids i aquests per tant, s'acumulen als residus. Les concentracions d'activitat d'aquests residus generalment no són gaire elevades, només en els casos de tractaments d'aigües subterrànies poden arribar a ser més elevades de 10 Bq/g. En els casos de tractaments d'aigües subterrànies, el radó es pot acumular a elevades concentracions d'activitat en els llocs de treball.

Producció d'energia geotèrmica

Les aigües geotèrmiques són un recurs força utilitzat per escalfar les llars, oficines, granjes, etc. Els fluids salins calents dels dipòsits geotèrmics poden tenir un contingut sòlid del 30%. La concentració mitjana de ^{226}Ra en aquest tipus de residus és al voltant d'uns 5 Bq/g.

Producció de ciment

En la producció de ciment s'utilitzen materials que poden contenir uns certs nivells d'urani i tori. Un dels elements utilitzats és el fosfoguix (19% del fosfoguix reprocessat, s'utilitza en la fabricació de ciment), així com també altres. L'activitat d'aquests materials de construcció pot arribar a valors de 0.25 Bq/g d'U i Th.

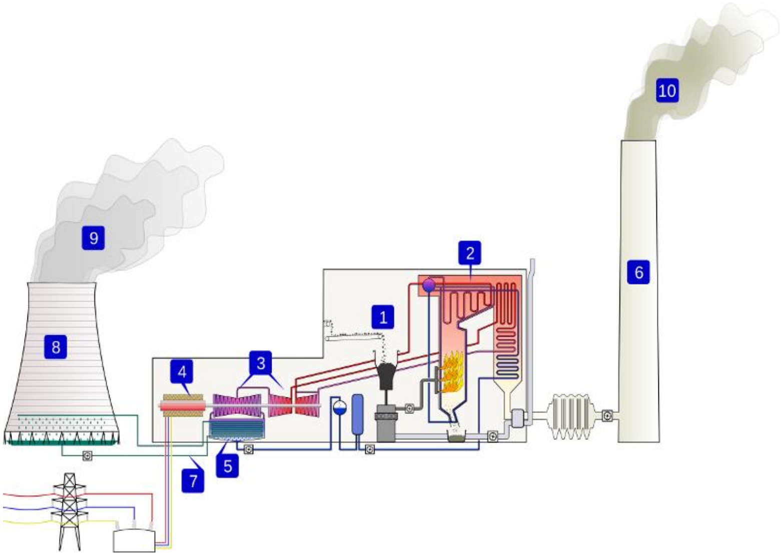
Si ens centrem en les indústries NORM que poden afectar la qualitat de l'aigua del riu Ebre, l'objecte d'aquest estudi són tres indústries. Anant des del naixement del riu Ebre cap a la desembocadura, les primeres indústries que ens trobem són les centrals tèrmiques de carbó, la segona indústria la trobem a l'embassament de Flix, aquesta és actualment una planta de producció de fosfat bicàlcic. Finalment, situada a uns 50 Km de Flix està l'estació de tractament d'aigua potable (ETAP), ubicada a l'Ampolla, on es potabilitza l'aigua del riu Ebre per abastir a tota la província de Tarragona.

A continuació, s'ha considerat adient fer una explicació detallada de les tres indústries NORM que hem comentat anteriorment que poden afectar a la qualitat de l'aigua del riu Ebre mitjançant els seus processos. Per aquest motiu, en el següents apartats es farà una revisió bibliogràfica sobre diferents aspectes relacionats amb la mesura i quantificació de la radioactivitat al voltant d'aquestes indústries.

1.2.2.1. Centrals tèrmiques de carbó

Inicialment es farà una breu descripció de les centrals tèrmiques de carbó, tot i que a la conca del riu Ebre estan a una distància considerable del riu i alguna d'elles, actualment sense activitat, van estar molts anys sent un motor imprescindible en la producció d'energia. És per això, que creiem adient considerar encara aquesta indústria en el nostre estudi.

Les centrals tèrmiques convencionals produeixen energia elèctrica a partir de combustibles fòssils com el carbó, fuel-oil o gas natural, mitjançant un cicle termodinàmic d'aigua-vapor. Independentment de quin sigui el combustible fòssil que utilitzen, l'esquema de funcionament de totes les centrals és pràcticament el mateix (Figura 1.4). Les úniques diferències són el pretractament del combustible abans de ser injectat a la caldera i el disseny dels cremadors.



1. Combustible
2. Caldera
3. Turbina
4. Alternador
5. Intercambiador de calor
6. Xemeneia
7. Aigua de refrigeració
8. Torre de refrigeració
9. Vapor d'aigua
10. Gasos de combustió

Figura 1.4. Esquema bàsic d'una central tèrmica convencional [38].

Centrant-nos en les centrals tèrmiques de carbó lignit, en el procés de combustió es generen restes (escòria del carbó i cendres volants) amb elevades concentracions d'activitat de radionúclids naturals, concretament els més abundants són ^{238}U, ^{230}Th, ^{226}Ra, ^{210}Pb, ^{210}Po, ^{232}Th, ^{228}Ra, ^{40}K. Les concentracions d'activitat dels subproductes es troben a més elevades concentracions que la matèria primera, per tant són les fonts més importants d'exposició de radionúclids naturals envers als treballadors i població. És per aquest motiu que d'acord amb la nova normativa *Basic Safety Standards* (BSS) [39], les centrals tèrmiques de carbó estan incloses a la llista d'indústries NORM i han de ser controlades per tal de classificar el potencial d'exposició dels treballadors i les poblacions, des de la perspectiva radiològica.

Aquest tipus d'indústria està present en diversos llocs geogràfics d'arreu del món, a la Taula 1.2 hi ha un recull de totes les activitats mitjanes dels principals radionúclids naturals (^{40}K , ^{226}Ra, ^{232}Th, ^{238}U, ^{210}Pb i ^{210}Po) de les centrals tèrmiques de carbó lignit. Pel que fa a la matèria primera, veiem gran variabilitat en les activitats, els valors van des de 9-346 Bq/kg, 9-19 Bq/kg i 36-173 Bq/kg pel que fa al ^{232}Th, ^{226}Ra i ^{40}K, respectivament. D'altra banda, si ens fixem amb les activitats dels subproductes de la combustió del lignit (cendres-volants i cendres de fons), veiem que presenten concentracions d'activitat més elevades que el propi carbó lignit. A més, en alguns casos podem veure que aquests subproductes presenten desequilibris entre els diferents radionúclids de les sèries de l'^{238}U i ^{232}Th. Per il·lustrar això, es pot esmentar l'estudi de Karangelos i col. [40] on es pot veure que els valors d'activitat dels radionúclids varien significativament en les cendres de fons (681 Bq/kg, 662 Bq/kg i 275 Bq/kg pel que fa a l'^{238}U, ^{226}Ra i ^{210}Pb, respectivament). En aquest estudi, s'avalua la relació entre les característiques radiològiques, la radioactivitat natural, la pertorbació de l'equilibri secular i la taxa d'exhalació del radó en les cendres recollides en diverses zones de la central. Els autors conclouen que l'equilibri secular dels radionúclids de la sèrie de l'^{238}U està significativament pertorbat degut a l'exhalació del radó i que es necessari fer els càlculs dosimètrics pertinents als voltants de la central tèrmica de carbó lignit per tal d'avaluar l'impacte sobre la població.

El ^{222}Rn és un gas radioactiu inert amb una vida mitjana de 3.82 dies, i un producte de desintegració del ^{226}Ra. Quan el ^{226}Ra es desintegra, els àtoms de ^{222}Rn són expulsats i transferits a les aigües subterrànies o a l'aire [41–43]. En relació amb l'exhalació del radó, diversos estudis se centren en controlar la presència de radó tant en residències properes a aquestes instal·lacions com en les cendres volants [44–50]. Per exemple, en l'estudi de Mahur i col. [47] es mesuren les taxes d'exhalació de radó en el carbó i les cendres volants d'una central tèrmica de Kolaghat (India). Els resultats d'aquest estudi

Taula 1.2 Concentracions dels radionúclids naturals al lignit, cendres de fons i volants en diferents regions.

Lloc	Tipus de mostra	^{40}K	^{226}Ra	^{232}Th	^{238}U	^{210}Pb	^{210}Po	Referències
Kosovo	Lignit	36 ± 8	9 ± 1	9 ± 3	-	-	-	[51]
	Centres de fons	195 ± 13	28 ± 3	34 ± 2	-	-	-	
	Cendres volants	133 ± 16	30 ± 3	30 ± 3	-	-	-	
Grècia	Lignit	173 ± 14	346 ± 2	19 ± 9	306 ± 4.2	361 ± 9.6	-	[40]
	Centres de fons	405 ± 11	662 ± 9	44 ± 5	681 ± 3.5	275 ± 5.9	-	
	Cendres volants	454 ± 11	64 ± 3	53 ± 5	964 ± 6.6	1158 ± 11	-	
Espanya	Lignit	104 ± 15	-	18 ± 3	-	-	-	[52]
	Centres de fons	235 ± 11	149 ± 6	66 ± 3	-	-	57 ± 7	
	Cendres volants	306 ± 13	191 ± 9	74 ± 3	-	-	257 ± 30	
Turquia	Lignit	123 ± 11	15 ± 2	11 ± 2	-	-	-	[53]
	Centres de fons	376 ± 9	50 ± 1	25 ± 2	-	-	-	
	Cendres volants	94 ± 28	149 ± 2	58 ± 4	-	-	-	
Serbia	Lignit	120	29	21	43	-	-	[54]
	Centres de fons	241	65	39	81	-	-	
	Cendres volants	360	120	72	129	-	-	

mostren que la taxa d'exhalació de radó a partir de les mostres de centres volants és més elevada que la de les mostres de carbó i a més la concentració de radionúclids en les cendres volants augmenta després de la combustió del carbó. Finalment, s'estima que la població que viu dins d'un radi de 80 Km de la central tèrmica pot estar exposada a dosis més elevades que la resta. En un altre estudi d'aquest mateix grup de recerca [48] s'avalua l'exhalació del radó en les cendres volants d'un altra central tèrmica de l'Índia, concretament a Durgapur. D'aquest estudi cal destacar que els autors veuen una certa correlació entre la taxa d'exhalació de radó i la concentració d'^{238}U, entre les concentracions d'activitat d'^{238}U i ^{232}Th i les concentracions d'activitat de ^{232}Th i ^{40}K.

Pel que fa a les mesures de radó a l'interior dels habitatges en zones on hi ha centrals tèrmiques, un exemple és l'estudi realitzat per Manousakas i col. [50] on mitjançant un detector SSNTD (*solid-state nuclear track detector*) s'avalua el radó a l'interior dels edificis de Grècia. Les mesures es duen a terme al llarg d'un any en quatre períodes consecutius de 3 mesos. Les concentracions d'activitat obtingudes de radó van estar molt per sota dels nivells d'acció recomanats per la Comissió Europea i la US EPA [55], tenint en compte les concentracions d'activitat de ^{226}Ra en el sòl i la baixa permeabilitat de la roca de fons de la zona.

Per altra banda, hi ha estudis enfocats en l'avaluació radiològica de la zona on hi ha presents centrals tèrmiques de carbó lignit [56,57]. Concretament, en l'estudi de Papadopoulos i col. [57] es determina l'activitat dels isòtops d'urani a les deposicions humides (aigua de pluja) de les proximitats d'una central tèrmica de lignit de Grècia. Les concentracions d'activitat d'^{238}U trobades van ser entre 2.2 ± 0.6 i 90 ± 14 mBq/L. Els autors van atribuir aquests valors a l'operació d'aquestes centrals i a les deposicions de cendres que produeixen. En canvi, en l'estudi de Zunic i col. [56] on s'avaluen 38 aigües al voltant d'una central tèrmica de lignit a Obrenovac (Sèrbia), es van obtenir concentracions d'activitat superiors. Les concentracions obtingudes van ser 0.2 - 27.1 mBq/kg de ^{226}Ra, 7.4 - 104.0 mBq/kg d' ^{234}U i 15.7 - 854.0 Bq/kg d' ^{238}U. Tot i això, els autors conclouen segons els valors d'activitat obtinguts, que no hi ha perill radiològic significant.

Donat que en diferents estudis s'ha pogut veure un impacte a la zona degut a l'operació de les centrals tèrmiques de carbó lignit, es va plantejar un estudi per tal d'avaluar la qualitat de les aigües del riu Martín, un dels afluents del riu Ebre. La conca del riu Martín, és una zona minera on s'extreien una gran varietat de metalls. Antigament, la producció de les conques mineres d'Aragó era de 238.4 Tm de coure, 922 Tm de plom i 3087 Tm de lignit. Actualment, només hi ha extracció de lignit i ferro.

Tot i això, el conjunt de la producció minera d'Aragó ha estat durant anys la primera productora nacional de lignit en les conques terolenses, sent la meitat del lignit extret a Espanya [58].

L'ús principal del carbó que s'extrau de les mines és com a combustible per a les centrals termoelèctriques de l'Aliga, Escatrón, Escucha i Andorra. La central tèrmica de carbó lignit d'Escucha va ser tancada fa pocs anys per ser la planta més contaminant d'Europa amb dotze milions de tones de CO_2 emetent-se a l'atmosfera.

Així doncs, el propòsit de l'estudi següent va ser avaluar la qualitat de les aigües tant potables com superficials de diferents punts de la conca del riu Martín donat que a més a més de tenir una zona lignifera de coves mineres, la seva conca presenta una gran variabilitat geològica i un gran nombre d'abocaments tant urbans com industrials que poden afectar a la qualitat de les seves aigües. Els paràmetres radiològics analitzats van ser l'índex d'alfa total i beta total, els isòtops d'urani (^{234}U, ^{235}U i ^{238}U), els isòtops de radi (^{224}Ra i ^{226}Ra) i el radó (^{222}Rn).

Donat que no es disposava de la metodologia al laboratori per a l'anàlisi del radó, es va realitzar un treball previ per tal de posar a punt el mètode. Cal remarcar que a la bibliografia no hi havia uniformitat sobre aquest procediment [59–62], així doncs es va dur a terme l'optimització del mètode, per tal d'evitar possibles interferències en el comptatge (selecció del líquid d'escintil·lació, volum de mostra). A fi de fer una validació, i tenint en compte que no hi ha patró de ^{222}Rn, s'ha utilitzat patró de ^{226}Ra (deixant-lo durant 21 dies abans de la mesura per tal que estiguin en equilibri secular). Finalment, per tal de verificar l'aplicabilitat d'aquest mètode, es va determinar el contingut de ^{222}Rn d'una aigua prèviament analitzada pel laboratori LARUC *(Laboratory of the University of Cantabria)*, laboratori de referència nacional i internacional pel que fa a les mesures de ^{222}Rn.

Després de la validació del mètode, aquest va ser aplicat a la determinació de ^{222}Rn en diferents fonts d'origen natural de diferents procedències, amb l'objectiu de tenir aigües de diferents geologies del terreny, tals com terreny granític, argilós, sorrenc, etc. Els resultats obtinguts en aquest estudi s'inclouen a l'Annex I i han estat publicats a la revista *Journal of Environmental Radioactivity 151 (2016) 275 – 281.*

Un cop optimitzat el mètode del ^{222}Rn, es va continuar amb l'estudi de la caracterització d'aigües de la conca del riu Martín. Amb tots els resultats obtinguts en aquest estudi, es va creure convenient fer un article de difusió per tal de posar en evidència les activitats dels diferents radionúclids avaluats. A continuació s'inclou l'article realitzat pel nostre grup de recerca juntament amb el personal del Consorci d'Aigües de Tarragona (CAT), publicat a la revista Tecnoaqua nº13 (2015) i anomenat "*Caracterización radiològica de las aguas de consumo humano en un afluente del río Ebro, el río Martín".* Aquest article dóna una visió l'activitat radiològica de l'aigua de consum d'onze poblacions de la conca del riu Martín, així com també d'alguns punts del riu, tenint en compte la legislació vigent.

1.2.2.1.1. Caracterización radiològica de las aguas de consumo humano en un afluente del río Ebro, el río Martín.

CARACTERIZACIÓN RADIOLÓGICA DE LAS AGUAS DE CONSUMO HUMANO EN UN AFLUENTE DEL RÍO EBRO, EL RÍO MARTÍN

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Resumen

En este artículo se presentan los resultados obtenidos en un estudio en el que se han determinado diferentes parámetros radioactivos (incluyendo la actividad de radón y la de algunos radionúclidos naturales como el uranio y el radio) tanto en las aguas superficiales del río Martín como en aguas destinadas al consumo humano procedentes de su área de influencia. Los resultados correspondientes a los índices de actividad de alfa total y beta total en las aguas destinadas al consumo han sido inferiores a los valores paramétricos establecidos en el Real Decreto 140/2003 y, por tanto, no representan una contribución significativa a la exposición de radiación por el consumo de agua potable. Las actividades de radionúclidos naturales como el ^{226}Ra y ^{238}U tampoco fueron significativas, por lo que se puede considerar despreciable el impacto sobre la salud de la población desde el punto de vista radiológico.

Palabras clave

Agua potable, agua superficial, parámetros radioactivos, radón, actividad industrial.

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1. Introducción

Los seres humanos están expuestos constantemente a radiación que puede tener origen natural o antropogénico. La importancia de controlar la exposición a la radiación se debe a que ésta puede interferir en las funciones vitales de las células y provocar toda una serie de efectos que pueden llevar a distintas manifestaciones corporales como son cánceres, tumores, efectos en embriones durante el embarazo, etc. Es importante indicar que las exposiciones a la radiación natural, que a su vez se puede clasificar como externa (cósmica y terrestre) o interna (ingestión e inhalación), son en general mucho más significativas que las exposiciones debidas a fuentes artificiales, excepto en radiodiagnóstico y en algunos tratamientos médicos.

Una de las fuentes de radiación interna a tener en cuenta es la debida a la ingestión de aguas de consumo. Según la legislación vigente, totas las aguas que se suministran a través de redes de distribuciones públicas o privadas tienen que cumplir con los valores paramétricos establecidos en el Real Decreto 140/2003 (en el que se establecen los criterios sanitarios de la

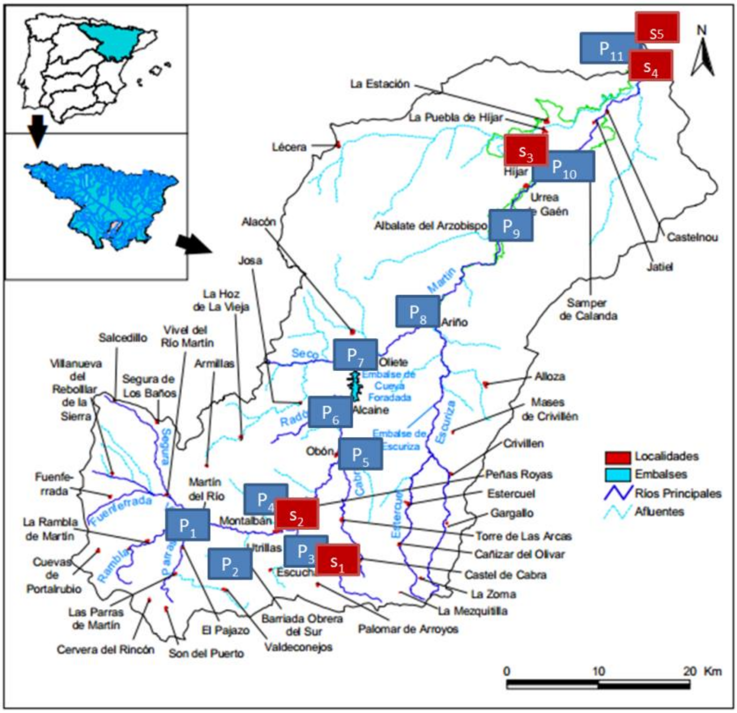

Figura 1. Puntos de muestreo en la Cuenca del río Martín: P = aguas de fuentes de poblaciones; S= aguas superficiales.

calidad del agua de consumo humano). En particular, los valores fijados en esta normativa para los parámetros radiactivos son de 0.1 Bq/L y de 1.0 Bq/L para los índices de actividad alfa total y beta resto respectivamente, 100 Bq/L para la actividad de tritio y 0.1 mSv/año para la dosis indicativa total. Además, organizaciones internacionales como la *World Health Organisation* [1] y la *United Nations Scientific Committee on the Effects of Atomic Radiations* [2] también remarcan la importancia de establecer normas sobre la calidad radiológica del agua. Algunos de los valores paramétricos recomendados por la WHO para los radionúclidos de origen natural son 10 Bq/L para ^{238}U, 1 Bq/L para ^{234}U y ^{226} Ra, y 0,1 Bq/L para ^{210}Po, ^{228}Ra y ^{210}Pb.

Cabe también mencionar que más recientemente se ha publicado una reglamentación europea que está pendiente de su transposición a España en la que se establecen los requisitos para la protección sanitaria de la población respecto a las sustancias radiactivas en las aguas destinadas al consumo humano [3]. Los valores paramétricos que se establecen en esta nueva directiva son los mismos que los incluidos en el Real Decreto 140/2003 con la diferencia de que se añade la actividad de radón (con un valor máximo de 100 Bq/L) como parámetro a determinar.

Las aguas superficiales y subterráneas son las más utilizadas como aguas que posteriormente se potabilizan para el consumo humano. Éstas pueden contener diferentes niveles de isótopos radioactivos cuyo origen generalmente está directamente relacionado con la geología del terreno en el que se encuentran o discurren las mismas, aunque también, algunas actividades industriales (minería, industrias del fosfato, etc.) pueden incrementar la presencia de radionúclidos en las aguas.

Una de las zonas singulares de nuestra península es la cuenca del rio Martín, un afluente del río Ebro que atraviesa tres grandes dominios geológicos: Dominio Central Ibérico, Dominio Maestrazgo-Catalánides y Depresión del Ebro. La cuenca del Río Martín presenta una zona lignífera, cuevas mineras y distintas centrales térmicas actualmente en funcionamiento que se abastecen directamente del río. La gran variabilidad geológica, la actividad industrial de la zona y los pocos datos publicados sobre el contenido radiológico de las aguas de este río fueron los motivos que impulsaron este estudio en el que determinaron los parámetros radiológicos (incluyendo la actividad de radón y las actividades de algunos radionúclidos naturales como el uranio y el radio) tanto en las aguas superficiales del río como en las destinadas al consumo humano procedentes de esta zona.

Tabla 1. Localización de los puntos de muestreo de la Cuenca del Río Martín y el número de habitantes de las distintas poblaciones.

ID	Localización	Coordenada SIGPAC		Nº habitantes
		Latitud	Longitud	
P_1	Martín del Río	40º50’38.8’’ N	0º53’47.8’’W	466
P_2	Utrillas	40º48’46.9’’ N	0º50’42.0’’W	3238
P_3	Escucha	40º47’40.7’’ N	0º48’40.3’’W	995
P_4	Montalbán	40º49’58.6’’ N	0º48’2.1’’W	1350
P_5	Obón	40º54’17.6’’ N	0º43’24.0’’W	39
P_6	Alcaine	40º57’11.5’’ N	0º42’18.0’’W	69
P_7	Oliete	40º59’52.4’’ N	0º40’25.3’’W	459
P_8	Ariño	41º1’49.3’’ N	0º35’35.1’’W	893
P_9	Albalate del Arzobispo	41º7’24.1’’ N	0º30’40.6’’W	2.087
P_{10}	Hijar	41º10’27.2’’ N	0º27’1.6’’W	1.806
P_{11}	Escatrón	41º17’18.5’’ N	0º19’27.6’’W	1.133
S_1	Escucha	40º47’40.7’’ N	0º48’40.3’’W	-
S_2	Montalbán	40º49’58.6’’ N	0º48’2.1’’W	-
S_3	Hijar	41º10’27.2’’ N	0º27’1.6’’W	-
S_4	Escatrón	41º17’10.9’’ N	0º18’51.2’’W	-
S_5	R. Ebre (Escatrón)	41º17’34.7’ N	0º19’03.5’’W	-

2. Toma de muestras

Se recogieron muestras de agua de consumo de once poblaciones de la Cuenca del Río Martín y cinco muestras de aguas superficiales del río. En la **Figura 1** se pueden ver los diferentes puntos de muestreo marcados como S (aguas superficiales) o P (poblaciones). En la **Tabla 1** se proporciona información detallada sobre estos diferentes puntos de muestreo.

Las aguas de consumo fueron recogidas en fuentes presentes en las distintas poblaciones con botellas de plástico de 2 L. Adicionalmente, se tomaron 100 mL con una botella de vidrio para el análisis del radón (^{222}Rn). Este radionúclido es un gas que puede estar disuelto en las aguas y para su correcto muestreo se tienen que seguir unas precauciones específicas. Concretamente, se deja correr el agua a velocidad lenta durante unos 3 minutos y posteriormente se coloca el recipiente de muestreo debajo del caudal de agua (evitando turbulencias). Cuando el recipiente está completamente lleno se coloca rápidamente el tapón y se cierra herméticamente. Es importante comprobar la ausencia de aire girando el recipiente boca abajo, y en caso que se observen burbujas de aire se debe repetir el muestreo. Finalmente, se anota la fecha y hora de recogida de la muestra.

3. Procedimientos de ensayo

En los siguientes apartados se comentan brevemente los procedimientos de ensayo utilizados en este estudio. En la **Tabla 2** se muestran los métodos, instrumentación, así como la actividad mínima detectable (AMD) para cada procedimiento de ensayo. Todos estos procedimientos están validados internamente y a través de la participación en ejercicios de intercomparación organizados por el Consejo de Seguridad Nuclear (CSN) y el Organismo Internacional de la Energía Atómica (IAEA). También es importante destacar que dos de los ensayos, concretamente los correspondientes a la determinación de los índices de actividad alfa total y beta total, están incluidos en el alcance de acreditación del laboratorio según la norma ISO 17025:2005.

3.1. Índices de actividad alfa y beta total

El índice de actividad de alfa total se determina utilizando dos métodos diferentes en función de la conductividad de las muestras. En los dos métodos las medidas se realizan en un contador de centelleo sólido de sulfuro de zinc durante 2000 minutos. Si la muestra tiene una conductividad inferior a 2000 µS/cm, el método utilizado es el que está descrito en el estudio de Palomo y col. [4] y consiste en la evaporación de alícuotas de 20 mL de cada muestra hasta casi sequedad para después transferir el concentrado a una plancheta de 5 cm de diámetro, secar bajo una lámpara y colocar encima un disco de sulfuro de zinc.

El segundo método está basado en la coprecipitación y se aplica a las

Tabla 2. Resumen de los métodos utilizados para determinar cada uno de los parámetros radioquímicos y la actividad mínima detectable (AMD) en Bq/L.

Parámetro	Procedimiento	Detección	AMD (Bq/L)
Índice alfa total	Evaporación (20mL) o coprecipitación	Det. Centelleo sólido de Sulfuro de zinc	0,025
Índice beta total	Evaporación (250mL o 40mL)	Contador proporcional alfa/beta	0,040
^{234}U, ^{235}U, ^{238}U	Resina UTEVA + electrodeposición (500mL)	Espectrometría alfa	0,001
^{224}Ra, ^{226}Ra	Coprecipitación con bario (500mL)	Det. Centelleo sólido de Sulfuro de zinc	0,001
^{222}Rn	10 mL muestra+ Ultima Gold F (12 mL aproximadamente)	Det. Centelleo líquido	2,000

muestras que presentan conductividades superiores a 2000 µS/cm. En este procedimiento, se filtran 500 mL de agua, se ajusta el pH a 7 y se añaden 20mL de H_2SO_4. Después, la muestra se calienta hasta que empieza a hervir, y se deja 5 minutos en estas condiciones. A continuación se deja enfriar a temperatura ambiente durante 1 hora para seguidamente calentar de nuevo otra vez hasta 50ºC. Finalmente se añade 1 mL de $BaCl_2$ (5mg/ml) y se mantiene a 50ºC durante 30 minutos. A continuación, se añade 1 mL de $FeCl_3$ (5mg/ml) y unas gotas de indicador de púrpura de bromocresol. Con el fin de obtener el pH correcto, se añade NH_4OH hasta que se vea coloración violeta. La muestra se mantiene a temperatura ambiente 30 minutos. Después de este tiempo, se filtra la muestra, y el filtro se pone en una plancheta hasta que quede seco. Una vez se ha secado el filtro en la plancheta se coloca encima un disco de sulfuro de zinc.

El método utilizado para determinar el índice de actividad beta total se basa en la norma UNE 73311-4:2002, y está descrito en el estudio de Palomo y col. [4] y es similar al primero de los dos métodos indicados para el índice de actividad alfa total. Éste también consiste en la evaporación de un cierto volumen de agua (entre 50 mL y 200 mL en función de la conductividad de las muestras) hasta casi sequedad para después transferir el concentrado a una plancheta de 5 cm de diámetro y secar bajo una lámpara. Las medidas se realizan durante 2000 minutos en un contador proporcional alfa/beta.

3.2. Determinación de los isótopos de uranio y radio

El método utilizado para medir los isótopos de uranio (^{238}U, ^{234}U y ^{235}U) está descrito en el trabajo de Mola y col. [5]. Brevemente, el método consiste en una precipitación de los actínidos y una separación del uranio utilizando una resina UTEVA (Triskem, Bruz, France). La solución resultante que contiene los isotopos de uranio es electrodepositada durante 2 horas, bajo un voltaje de 1.5 A/cm^2. Un minuto antes de finalizar la electrodeposición, se añade 1 mL de hidróxido de amonio concentrado, para asegurar que se fije el uranio a las planchetas de acero. La recuperación del procedimiento se calcula añadiendo una cantidad conocida de trazador de ^{232}U a la muestra antes de iniciar el ensayo. La medidas se realizaron en un espectrómetro alfa Ortec durante 4000 minutos.

Para la determinación de ^{226}Ra y ^{224}Ra, se utiliza un método de coprecipitación con una sal de bario. Este procedimiento implica una precipitación utilizando cloruro de bario y ácido sulfúrico. Se ajusta el pH, y finalmente el precipitado de sulfato de bario /sulfato de radio formados son depositados en una plancheta para la medida en el detector de sulfuro de zinc durante 1000 minutos.

3.3. Determinación de Radón

El método para la determinación de radón está descrito en el estudio de Fonollosa y col. [6] y consiste en coger 10 mL de la muestra de agua para mezclarla con el líquido de centelleo (Ultima Gold F) hasta llenar un vial de 20 mL de polietileno con una capa de teflón en la parte interior del mismo. Es importante en esta etapa asegurar la ausencia de aire en el recipiente. Luego se agita vigorosamente y se deja estabilizar durante cuatro horas antes de las medidas que se realizan en un detector de centelleo líquido Quantulus 1220 de Perkin Elmer durante dos ciclos de 500 minutos.

4. Resultados

Los resultados obtenidos para los diferentes parámetros radioactivos se muestran en la **Tabla 3** y en ellos se puede ver que los de los índices de actividad alfa total en las aguas de consumo varían entre <0,02 y 0,06 Bq/L mientras que en las aguas superficiales los valores son ligeramente superiores y varían entre 0,05 y 0,31 Bq/L. Así,

Tabla 3. Índices de actividad alfa total y beta total, actividades de radio, uranio y radón en las muestras de agua procedentes de la cuenca del Río Martín. Nota: ^{1}Restando la contribución del ^{40}K (Índice de actividad beta resto); ^{2}Un miligramo (mg) de uranio natural contiene 12,3 Bq de U-238.

Muestra	Potasio (mg/L)	Índice alfa (Bq/L)	Índice beta^{1} (Bq/L)	Ra-226 (mBq/L)	Ra-224 (mBq/L)	Uranio^{2} (µg/L)	U-238 (mBq/L)	U-234 (mBq/L)	Radón (Bq/L)
Valores paramétricos		**0,1**	**1**	**500**			**300**	**280**	**100**
AP$_{1}$	1,2	0,05	0,05	2	7	1,1	13	18	<1,0
AP$_{2}$	0,9	0,03	0,04	4	2	0,7	8,1	12	<1,0
AP$_{3}$	0,8	<0,02	<0,03	4	12	0,5	6,5	14	<1,0
AP$_{4}$	0,8	<0,02	0,06	<2,4	4	1,4	17	24	1,84
AP$_{5}$	1,7	0,03	0,1	6	3	0,1	1,4	2,1	0,91
AP$_{6}$	2,2	0,04	0,12	23	<1,65	0,1	1,6	2,8	< 1,0
AP$_{7}$	0,8	0,04	<0,03	<2	2	0,1	1,4	1,9	<1,0
AP$_{8}$	3,1	0,03	0,14	8	4	0,1	1,5	1,9	2,59
AP$_{9}$	16,5	0,05	0,55	<2,1	3	0,2	2,7	4,2	<1,0
AP$_{10}$	4,6	0,06	0,2	12	<2,5	0,2	2,8	4,4	<1,0
AP$_{11}$	4,4	0,04	0,17	5	<1,4	3,3	40,2	49,7	<1,0
AS$_{1}$	10,2	0,05	0,37	6	3	0,2	3	3,9	<1,0
AS$_{2}$	4,8	0,07	0,21	4	3	0,2	2,4	2,7	< 1,0
AS$_{3}$	6,5	0,21	0,33	14	6	1,5	18,8	24,9	< 1,0
AS$_{4}$	13,2	0,31	0,53	23	3	11,8	145,7	197,9	< 1,0
AS$_{5}$	4,3	0,18	0,34	20	16	1,4	17,3	21,9	<1,0

mientras las aguas de consumo no superan en ningún caso el valor máximo establecido para este parámetro en el Real Decreto 140/2003 (0.1 Bq/L) en algunas de las aguas superficiales si se supera aunque en ningún caso los valores obtenidos son muy elevados. En el caso del índice de actividad beta total para las aguas de consumo este parámetro varía entre <0,03 y 0,55 Bq/L y en las aguas superficiales entre 0,21 y 0,53 Bq/L.

Es importante indicar que el ^{40}K, un isótopo radioactivo que se encuentra en una proporción del 0.0018% del potasio natural, es el responsable de la mayor parte de actividad beta observada en los índices de actividad beta total. Este dato queda confirmado por la correlación existente entre los valores de índice de actividad beta total y la concentración de potasio de las muestras (en ppm) y que se muestra en la **Figura 2a**. Es importante indicar que el Real Decreto 140/2003 establece un valor máximo de 1 Bq/L para el índice de actividad beta resto, que es el resultado de restar la contribución del ^{40}K al índice de actividad beta total, y en ninguna de muestras analizadas se supera.

Además de los índices de actividad alfa total, se consideró interesante determinar las actividades de uranio y radio ya que en los casos en los que el valor del índice de actividad alfa total supera

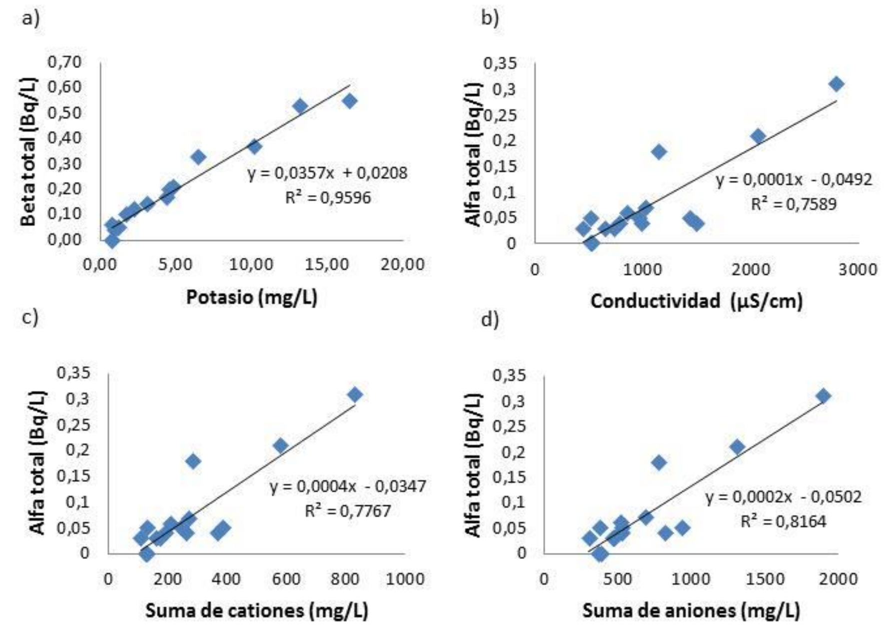

Figura 2. a) Índice beta total vs concentración de potasio; b) Índice alfa total vs conductividad; c) Índice alfa total vs suma de cationes; d) Índice alfa total vs suma de los aniones.

los 0.1 Bq/L se debe determinar la dosis indicativa total teniendo en cuenta las actividades de los radionúclidos que están presentes en el agua. El uranio y el radio son emisores alfa y, generalmente, son los que presentan una mayor contribución a los valores de los índices de actividad alfa total. Así, tal y como se observa en la **Tabla 3**, en las aguas potables las actividades del ^{226}Ra y ^{238}U varían entre 2-23 y 1,4-40,2 mBq/L mientras que en las aguas superficiales oscilan entre 4-23 y de 3-145,7 mBq/L, respectivamente.

Cabe señalar que los valores más altos de actividad para estos isótopos se localizan en el punto S_4 (Escatrón) justo donde desemboca el Río Martín al Río Ebro. Esta muestra es la que presentó también un mayor índice de actividad alfa total (0.31 Bq/L). Sin embargo, tanto en el caso de las aguas de potables como superficiales, incluyendo el punto S_4, los valores de actividad obtenidos para estos radionúclidos naturales están por debajo del límite establecido para ellos, 0.5 Bq/L para el ^{226}Ra y 3 Bq/L para el ^{238}U, teniendo en cuenta que la dosis indicativa total no debe superar los 0.1 mSv/año [3].

Estos valores son comparables a los presentados un estudio anterior [7], donde se determinó la radiactividad natural en las aguas superficiales de los afluentes de la parte derecha del Río Ebro, analizando los ríos Jalón, Martín y Guadalope y donde los autores concluyen que los valores de radioactividad natural encontrados se pueden atribuir a la minería del carbón y a las centrales térmicas, porque la extracción de este material incrementa la incorporación de radionúclidos en el agua superficial.

Los resultados sobre la determinación del radón también se incluyen en la **Tabla 3**. A pesar de que el radón (^{222}Rn) es un gas radiactivo que se produce en la cadena de desintegración del ^{238}U, los valores obtenidos no están correlacionados con los valores de los índices de actividad alfa total, ^{238}U ni ^{226}Ra. En todo caso, para ninguna de las muestras analizadas se superan los 100 Bq/L y estos resultados son coherentes con la bibliografía teniendo en cuenta que, en las aguas superficiales, el contenido de radón es bajo debido al corto periodo de desintegración del radón (3.8 días) y que la aireación a la que se ve sometida el agua en los ríos facilita la emisión del radón al aire. La concentración en estas aguas suele ser inferior a 2 Bq/L [8] Las aguas subterráneas, en cambio, pueden entrar en contacto con el radón proveniente de las rocas y solubilizarlo lo que explica que las concentraciones de radón en este tipo de aguas, dependiendo de las características geológicas del terreno, pueda llegar a alcanzar valores de actividad más elevados. Las actividades de radón pueden oscilar entre 5 y 50 Bq/L para areniscas, limos, arcillas o calizas pero estos valores pueden llegar a ser

La evaluación inicial del contenido radiactivo de las aguas de consumo de las once poblaciones situadas en la Cuenca del río Martín se ha realizado con éxito. En todos los casos, los índices de actividad de alfa total y beta total en las aguas destinadas al consumo han sido inferiores a los valores paramétricos establecidos en el Real Decreto 140/2003 y, por tanto, no representan una contribución significativa a la exposición de radiación por el consumo de agua potable

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superiores a 1000 Bq/L si el agua está en contacto con rocas con elevados contenidos de ^{238}U como algunos granitos. Esto se debe a la naturaleza gaseosa del ^{222}Rn que le aporta una gran movilidad y le permite emigrar desde los lugares de origen (materiales de la corteza terrestre que contienen ^{226}Ra y ^{238}U), a través de poros y grietas. En lo que respecta a la correlación existente entre los resultados obtenidos para los parámetros radioquímicos y los físico-químicos en las aguas potables y superficiales de la cuenca del Río Martín se han realizado una serie de representaciones gráficas que se muestran en la **Figura 2**. Así, en la **Figura 2a** se puede ver que los valores de índice de actividad beta total, están totalmente correlacionados con las concentraciones de potasio tal y como ya se ha mencionado anteriormente. En la **Figura 2b** se muestra la relación existente entre el índice de actividad alfa total y la conductividad de las muestras. Esto se debe a que una mayor conductividad indica una mayor presencia de sales en la muestras, algunas de ellas de ^{238}U, ^{234}U y ^{226}Ra, lo que a su vez aumenta el contenido radiactivo de las aguas y en este caso los índices de actividad alfa total. Finalmente en las **Figuras 2c** y **2d** se han representado gráficamente y por separado la suma de las concentraciones de aniones y cationes frente al índice de actividad de alfa total, obteniendo también en ambos casos, como era de esperar, una correlación bastante elevada por los mismas causas que explican la relación entre índice de actividad alfa total y conductividad.

5. Conclusiones

La evaluación inicial del contenido radiactivo de las aguas de consumo de las 11 poblaciones situadas en la Cuenca del Río Martín se ha realizado con éxito. En todos los casos, los índices de actividad de alfa total y beta total en las aguas destinadas al consumo han sido inferiores a los valores paramétricos establecidos en el Real Decreto 140/2003 y por tanto no representan una contribución significativa a la exposición de radiación por el consumo de agua potable. Las actividades de radionúclidos naturales como el ^{226}Ra y ^{238}U tampoco fueron elevadas por lo que se puede considerar despreciable el impacto sobre la salud de la población desde el punto de vista radiológico.

Por otro lado, los valores de actividad de radón obtenidos no están relacionados directamente con las actividades de ^{226}Ra presentes en las aguas superficiales y potables debido a su corto periodo de desintegración, a su gran movilidad y a su facilidad para emigrar desde los lugares de origen por su naturaleza gaseosa. Por otra parte, la relación observada entre los parámetros radioquímicos (índices de actividad alfa y beta total) y físico-químicos (con conductividad, concentración de aniones y cationes) puede ser útil para prever la necesidad de determinar los parámetros radiactivos a partir de los resultados obtenidos mediante ensayos de uso más habitual en los laboratorios.

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1.2.2.2. Indústria de producció de fosfat bicàlcic

En aquest apartat es farà una breu descripció de la indústria de producció de fosfat bicàlcic. Concretament, a la conca del riu Ebre, a l'altura de Flix, hi trobem un complex industrial anomenat Sociedad Electroquímica de Flix (actualment Ercros). Aquesta indústria en els seus orígens es basava en la producció de clor, més tard va començar la producció de fosfat bicàlcic destinat a la fabricació de pinsos per animals (la qual queda avui en dia).

El fosfat bicàlcic $Ca(H_2PO_4)_2$ és un suplement alimentari inorgànic, recentment classificat com a material d'alimentació, que conté un 18% de fòsfor i entre el 25-30% de calci, que resulta un complement òptim de fòsfor i calci en l'alimentació dels animals domèstics. Hi ha dues rutes per a la producció de fosfat bicàlcic: neutralització de l'àcid fosfòric desfluorat amb calci i la digestió de la roca fosfòrica amb àcid clorhídric. En particular a la planta de Flix, el procés de producció de fosfat bicàlcic es fa mitjançant la digestió de la roca fosfòrica amb àcid clorhídric [63] (Figura 1.5).

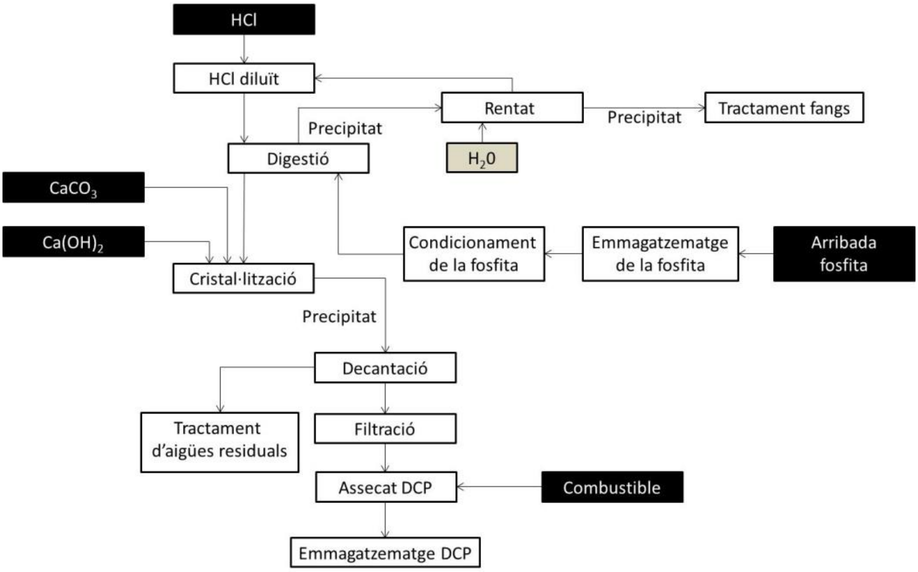

Figura 1.5. Esquema del procés de producció de fosfat bicàlcic amb àcid clorhídric [63].

Hi ha un altre punt geogràfic a l'estat espanyol, on hi ha també aquest tipus d'indústria NORM, concretament a Huelva. Aquesta ciutat, posseeix un dels complexos industrials més grans d'Europa, incloent empreses de fertilitzants, fosfoguixos, etc. Degut a l'alt índex de mortalitat, de malalties respiratòries i de càncer a la província, es va obrir una investigació on es va mostrar que existien abocaments il·legals tant a l'atmosfera com al medi marí per part d'aquestes indústries. Per aquest motiu l'any 2010, l'Audiència Nacional va obligar a les indústries involucrades a acabar amb l'abocament dels residus contaminats.

Des del punt de vista radiològic, s'han fet estudis per veure la concentració d'activitat de diferents radionúclids als estuaris dels rius Tinto i Odiel (Huelva) on es troben les basses residuals de fosfoguix [4,64–67]. Per exemple, en l'estudi de Villa i col. [65] es mostren les activitats d' ^{238}U durant 1989, 1999, 2001 i 2005 dels sediments dels rius Tinto i Odiel. A l'Odiel, les concentracions d'activitat d'^{238}U comencen amb una mitjana de 713.8 Bq/kg al 1989 fins a 228.4 Bq/kg al 2005. En canvi, al Tinto, la variació durant els anys és menyspreable, els resultats varien de 254.4 a 200 Bq/kg. Els autors conclouen que fins al 1989 hi havia una elevada concentració, en canvi després de 1998, degut a la clausura dels abocaments, les concentracions d'activitat van disminuir força, encara que les concentracions d'activitat no són les d'un riu no contaminat.

Després de la investigació de Huelva, el Departament de Medi Ambient de la Generalitat de Catalunya va encarregar al CSIC *"Consejo Superior de Investigaciones Científicas"* un informe sobre els contaminants als sistemes aquàtics continentals de Catalunya. En aquest marc, es va abordar un estudi dels sediments acumulats a l'embassament de Flix procedents del complex químic. En aquest estudi es va posar en manifest la presència de mercuri i altres metalls pesants d'elevades concentracions. Tot i això, no es va actuar fins que al 2001 es va donar un episodi de mortalitat de peixos a l'altura de la Central Nuclear d'Ascó. Immediatament, les Administracions Hidràuliques van analitzar diferents mostres d'aigua en les que es va detectar un alta concentració de mercuri. Aquest fet va crear una alarma social que va desembocar amb la publicació d'un estudi del CSIC i la Universitat de Barcelona (2004). Així, es va constatar l'acumulació de fangs contaminats al pantà de Flix amb concentracions elevades de metalls pesants i compostos organoclorats. Com a novetat, en aquest estudi es va posar en manifest la presència d'uns nivells de radioactivitat elevats (procedents de la cadena de desintegració de l'urani).

Amb tots els valors obtinguts en els estudis descrits anteriorment es va aprovar un projecte de descontaminació de l'embassament, que consistia en l'extracció, tractament, transport i disposició dels fangs en un abocador, el qual esta previst de finalitzar aquest 2016. Primer es va construir un mur de 1.4 quilòmetres de longitud i de doble línia, reblert amb material inert a l'interior, per aïllar els residus del cabal del riu. Així es manté el flux del riu pel marge esquerre de l'embassament i en cas de que es produís una incidència durant les obres, el mur impediria l'arrossegament dels sediments aigües avall (Figura 1.6). Després, al marge dret es va construir una planta de tractament que consta de diferents equipaments de cribat i hidrociclons per facilitar la classificació granulomètrica dels sediments (per mides i assecat). El material amb més contingut d'aigua es deshidrata amb tres filtres premsa i un cop assecat es trasllada junt a la resta de sòlids on són tractats en funció de les concentracions dels contaminants. Finalment, els fangs un cop tractats són traslladats a l'abocador del Racó de la Pubilla on es mantenen confinats. En aquest abocador, els residus es van impermeabilitzant mitjançant capes d'argiles i làmines impermeabilitzants de grans espessors. Fins i tot les aigües del procés són tractades en una planta depuradora (EDAR) mitjançant tècniques de floculació, precipitació, sedimentació i absorció en filtres de sorra i carbó actiu.

Figura 1.6. Dalt: complex industrial Ercros amb el mur de contenció, Baix esquerra: Racó de la Pubilla, Baix dreta: mur de contenció [68].

Des del punt de vista radiològic, al llarg de la història s'han fet diferents estudis en aquesta indústria. Un exemple és l'estudi publicat per Casacuberta i col. [69], on es determinen les concentracions d'activitat especifiques d'^{238,234}U, ^{230}Th, ^{226}Ra, ^{210}Pb i ^{210}Po en diferents punts de la indústria de fosfat bicàlcic. Pel que fa a la matèria primera, la fosforita, es van obtenir condicions d'equilibri secular en els radionúclids determinats (al voltant de 1700 Bq/kg d'^{238,234}U, ^{230}Th, ^{226}Ra, ^{210}Pb i ^{210}Po). En canvi, a les línies de producció les concentracions d'activitat van variant, fins a valors molt elevats en l'escòria formada al digestor (valors fins a $150 \cdot 10^3$ Bq/kg). Un estudi posterior d'aquest mateix grup de recerca [2] mostra les activitats de dues mostres de fangs procedents del procés industrial de producció de fosfat bicàlcic, que contenen 5036 ± 7 Bq/kg i 3993 ± 1 Bq/kg d'^{238}U, 6287 ± 6 Bq/kg i 5216 ± 4 Bq/kg d'^{234}U i 10090 ± 8 Bq/kg i 8618 ± 4 Bq/kg de ^{232}Th. Cal remarcar arran dels resultats dels dos estudis que respecte als valors obtinguts en la matèria primera [69], podem veure una clara preconcentració dels diferents radionúclids.

Addicionalment, durant el 2011 Mola i col. [3] van fer un estudi per poder veure l'impacte radiològic ambiental evident causat pel procés de concentració de radionúclids naturals durant l'elaboració del fosfat bicàlcic d'aquesta mateixa indústria. En aquest treball s'estudien els fangs de dues zones afectades pels abocaments incontrolats, davant la planta de fosfat bicàlcic i davant la planta de tractament d'aigües residuals, a diferents profunditats. Els resultats mostren que els fangs dels primers metres són el que presenten concentracions d'activitat més elevades, en concret els de la zona de davant la planta de fosfat bicàlcic presenten valors de 5847 ± 97 i 2499 ± 606 Bq/kg pel que fa al ^{226}Ra i ^{210}Pb, respectivament.

Aquest tipus d'indústria també està present en altres llocs fora de l'estat espanyol, concretament a Síria on utilitza roca fosfòrica de Síria [1,70]. A l'estudi de Attar i col. [1] es mostra una preconcentració als fangs respecte la matèria primera. Les activitats d'^{238}U i ^{226}Ra a la matèria primera són 517 i 353 Bq/kg, respectivament, mentre que als fangs són de 1039 i 208 Bq/kg. Contràriament, en l'estudi de Gäfvert i col. [70] no es veu cap efecte de preconcentració en els fangs, tot i que la matèria primera té el mateix origen. Les concentracions d'activitat mitjanes obtingudes en la matèria primera (roca fosfòrica) van ser de 837 Bq/kg pel que fa a l'^{234,238}U, ^{230}Th, ^{226}Ra, ^{210}Pb, ^{210}Po i als fangs de 178 ± 14 , 170 ± 14, 409 ± 8, 142 ± 4, 100 ± 5 Bq/kg (pes sec) per a l'^{238,234}U, ^{230}Th, ^{226}Ra i ^{210}Pb, respectivament.

A més a més, hi ha d'altres estudis que se centren en l'avaluació de l'impacte d'aquest tipus d'indústries a l'àrea geogràfica on es troben [71–74]. És un exemple l'estudi de de Bituh i col. [73] on es mesuren les concentracions d'activitat de radionúclids naturals (^{238}U, ^{226}Ra, ^{228}Ra i ^{40}K) a l'àrea on hi ha present una indústria de fertilitzants de fosfat (Croàcia). Aquest estudi se centra en veure els riscs per a la població, especialment per la ingestió d'aigua procedent de pous de la zona. Els resultats obtinguts indiquen que l'aigua subterrània de la zona presenta valors de dosi de 5.3 ± 1.3 μSv (pel que fa al ^{226}Ra), és a dir sota els límits (0.1 mSv), per tant, els efectes sobre la població, són negligibles. Tot i això, els autors recomanen fer un monitoratge periòdic pel tal de veure si l'àrea continua sense afectació radiològica.

Un altre exemple és l'estudi de Vandenhove i col. [72], en el que han realitzat una avaluació preliminar de la contaminació ambiental resultant de les activitats de cinc plantes de fertilitzants de fosfat ubicades a Bèlgica, Espanya, Síria, Egipte i Brasil. Aquestes plantes han estat escollides donat que hi ha poca informació sobre les concentracions d'activitat de radionúclids naturals a l'àrea geogràfica on es troben. En tots els llocs avaluats, les activitats dels isòtops de ^{226}Ra i ^{210}Po han estat els que presenten valors més elevats i per tant els que contribuiran més a la dosi total. De totes maneres, els autors d'aquest estudi conclouen que es necessita una investigació més profunda per tal de demostrar si la fauna està en risc en situacions de radioactivitat natural elevada.

En resum, amb aquesta síntesi bibliogràfica s'ha pogut veure que les elevades activitats de la matèria primera de la indústria de fosfat bicàlcic de Flix [69] ocasionen que hi hagin unes activitats elevades en els residus, subproductes i el terreny de l'entorn d'aquesta indústria [3]. A més, també s'ha pogut veure en altres estudis, la necessitat de fer monitoratges a l'àrea on hi ha presents aquest tipus d'indústries i sobretot, la importància de controlar les aigües subterrànies.

1.2.2.3. Estació de tractament d'aigua potable (ETAP)

Una altra de les indústries classificades com a NORM, són les estacions de tractament d'aigua potable (ETAP). A diferència de la indústria de fosfat bicàlcic esmentada l'apartat anterior, l'ETAP elimina els radionúclids que hi ha a l'aigua, generant fangs que contenen els radionúclids eliminats. Concretament, a la conca del riu Ebre a final dels anys setanta es va construir l'estació de tractament d'aigua potable a l'Ampolla, degut a l'escassetat d'aigua a les comarques de Tarragona provocada per la creació del complex químic de Tarragona i el creixement urbanístic i d'explotacions agrícoles. Aquesta planta, potabilitza l'aigua procedent del riu Ebre abastint a tota la província de Tarragona, concretament 61 municipis i 26 indústries.

El procés utilitzat en la planta potabilitzadora d'aigua de l'Ampolla està reflectit a la Figura 1.7. Els passos més importants són: coprecipitació amb clorur fèrric ($FeCl_3$), decantació de les partícules en suspensió, filtració a través de filtres de sorra i de carbó i finalment la cloració.

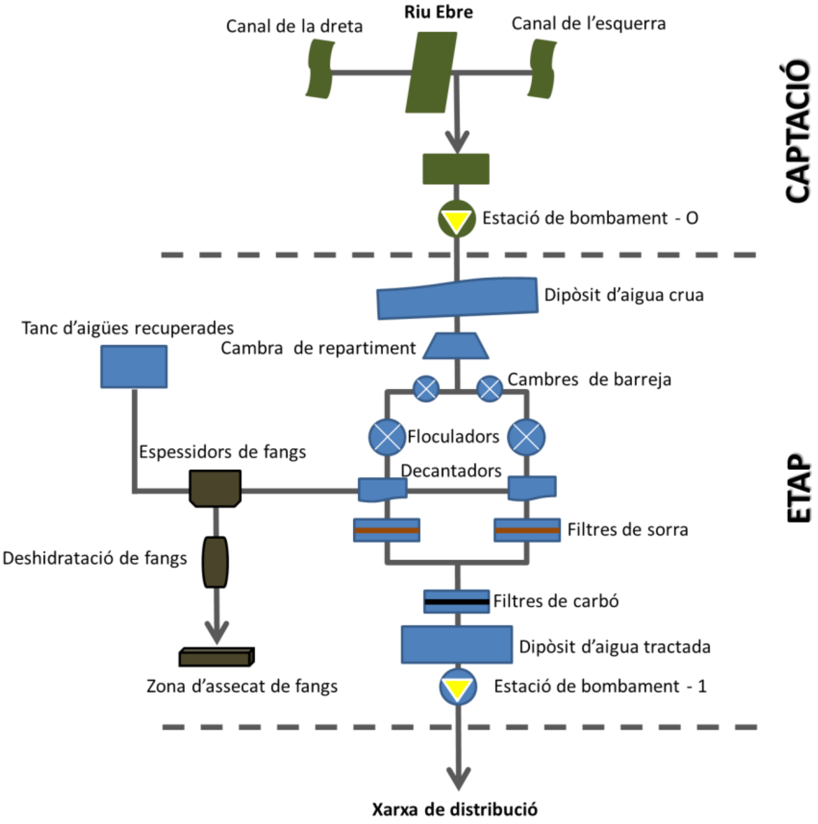

Figura 1.7. Seqüència de tractament de l'ETAP de l'Ampolla [75].

Cal destacar del procés de tractament, que quan es decanta l'aigua es dipositen els flocs al fons en forma de fangs, els quals contenen de forma preconcentrada tot tipus de compostos (radionúclids, compostos orgànics i inorgànics, etc.) que transporta l'aigua del riu. Llavors aquests fangs són recollits i una vegada concentrats són enviats una part a la centrifuga de deshidratació i una part al propi procés (floculadors). El fang no utilitzat en el procés, es deshidrata utilitzant centrífugues d'alt rendiment i s'envia als erols d'assecament (Figura 1.8).

Figura 1.8. Erols d'assecament dels fangs [75].

El principal problema de les plantes de tractament d'aigua és que els processos dissenyats per potabilitzar l'aigua concentren les radionúclids als filtres o fangs. Així doncs, els residus concentrats (fangs residuals i altres residus) requereixen un apropiat emmagatzematge. Per tant, les plantes de tractament d'aigua potable són considerades com a indústries productores de material NORM. Fins i tot, en els casos on les concentracions d'activitat de radionúclids als fangs són inferiors als valors legislats, el tractament d'aigua pot ocasionar l'acumulació de material NORM [34]. Per tal de donar més informació sobre aquest aspecte, hi ha un estudi realitzat per Palomo i col. [76] on s'avaluen diferents plantes de tractament (d'aigua potable, residuals o industrials) per tal de veure si es poden considerar indústries productores de material NORM. Els resultats mostren que els fangs produïts pel tractament de l'aigua concentren el material radioactiu de l'aigua. Aquest material procedeix generalment de la geologia del terreny, però les activitats industrials també poden tenir una influència important.

Des del punt de vista radiològic, a l'ETAP de l'Ampolla durant un període de sis anys (2002 - 2007) es va avaluar la capacitat d'eliminar radionúclids naturals i artificials [77]. Es va fer l'anàlisi d'alfa total, beta residual i triti de les aigües d'entrada i sortida. Els resultats mostren que els radionúclids s'eliminen al voltant d'un 20 % per emissors alfa i d'un 5% pels beta (el triti no s'elimina). Tot i això, els resultats obtinguts per a tots aquests paràmetres van ser sota els límits establerts a la legislació pel consum humà. Amb tots els resultats obtinguts durant els sis anys, els autors conclouen que en les mostres de fangs es veuen concentrats els radionúclids que estan presents a l'aigua d'entrada, i que la major contribució de radioactivitat als fangs procedeix de fonts naturals.

Hi ha d'altres estudis basats en obtenir una relació entre l'eliminació dels isòtops que poden estar presents a l'aigua d'entrada de la planta i el tractament utilitzat. Per exemple, Gäfvert i col. [78] i Baeza i col. [79] demostren que l'activitat d'alguns radionúclids de les cadenes de semidesintegració de l'urani i tori s'associa amb les partícules que s'eliminen de l'aigua durant els tractaments de sedimentació (després de l'adició d'un coagulant, com és el clorur de ferro (III)). Per exemple, en l'estudi de Baeza i col. [79], s'utilitza una planta pilot per provar l'efecte de quatre coagulants diferents. En aquest estudi, es va demostrar també que a part de la influència dels coagulants, també influeix el pH. En aquest sentit, els autors van obtenir el millor rendiment per a l'eliminació de l'urani en tots els casos a un pH de 6, independentment del tipus de coagulant utilitzat. En canvi, en el cas del radi, l'eliminació més elevada es va donar amb valors de pH bàsic, en aquest cas l'ús de diferents coagulants té una influència diferent (l'eliminació més elevada es va obtenir amb coagulants de ferro).

En els últims anys, en algunes ETAPs s'ha estudiat la incorporació d'una nova etapa en el procés de tractament d'aigua, l'osmosi inversa. Aquesta, té la capacitat d'eliminar compostos inorgànics i radionúclids dissolts a l'aigua després de totes les etapes del tractament [80–83]. L'estudi més novedós en relació a aquest tema està basat en la reducció de les concentracions d'activitat de radionúclids d'origen natural (^{238}U, ^{234}U, ^{226}Ra i ^{210}Pb) amb el tractament d'osmosi inversa de 21 pous subterranis de Chennai i Secunderabad (India) [83]. Donada la localització geogràfica, aquesta aigua subterrània presenta unes activitats de 40.9, 1.7, 41.5, 84.5, 100.1, i 17.0 mBq/L d' ^{234}U, ^{235}U, ^{238}U, ^{226}Ra, ^{228}Ra i ^{210}Pb, respectivament; els quals són eliminats durant el procés obtenint unes activitats sota els límits de detecció en tots els casos (<1.3 mBq/L). Els autors conclouen que el 97% i el 95% dels isòtops d'urani i radi són eliminats durant el tractament d'osmosi inversa.

Per tal d'aportar més informació radiològica de les anàlisis en les plantes de tractament d'aigua potable, s'adjunta a continuació l'article realitzat pel nostre grup d'investigació, publicat a la revista: *Journal of Environmental Radioactivity*, anomenat: "Presence of radionuclides in sludge from conventional drinking water treatment plants. A review". En aquest article es dóna una visió actual dels diferents estudis de la bibliografia enfocats a la influència dels tractament de les ETAPs i l'anàlisi radiològic de fangs. A més, també s'aporten les principals estratègies per reutilitzar aquests fangs (incloent per exemple l'aplicació directa en l'agricultura, i l'ús en materials de construcció entre d'altres).

1.2.2.1.1. Presence of radionuclides in sludge from conventional drinking water treatment plants. A review

PRESENCE OF RADIONUCLIDES IN SLUDGE FROM CONVENTIONAL DRINKING WATER TREATMENT PLANTS. A REVIEW

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Abstract

The analysis of sludge samples generated during water treatment processes show that different radioisotopes of uranium, thorium and radium, among others can accumulate in that kind of samples, even the good removal rates obtained in the aqueous phase (by comparison of influent and effluent water concentrations). Inconsequence, drinking water treatment plants are included in the group of Naturally Occurring Radioactive Material (NORM) industries. The accumulation of radionuclides can be a serious problem especially when this sludge is going to be reused, so more exhaustive information is required to prevent the possible radiological impact of these samples in the environment and also on the people. The main aim of this review is to outline the current situation regarding the different studies reported in the literature up to date focused on the analysis of the radiological content of these sludge samples from drinking water treatment plants. In this sense, special attention is given to the recent approaches for their determination. Another important aim is to discuss about the final disposal of these samples and in this regard, sludge reuse (including for example direct agricultural application or also as building materials) are together with landfilling the main reported strategies.

Keywords: sludge, NORM industry, drinking water treatment plant.

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1. Introduction

The radiological characteristics of the sludge samples generated in drinking water treatment plants (DWTP) are dependent on different factors as the source water type, and in this sense the geology and also the industrial activities of the areas where these plants are located are key parameters. Another important factor which can influence is the treatment that is applied over water samples (coagulation, flocculation, decantation and sand filtration). In the literature, there are different studies focused in the radiological characterisation of this kind of samples and this is of special importance since in most cases a common practice in DWTP facilities is the landfilling disposal of the sludge generated during the process, and in this case the health of the workers against the dangers arising from ionizing radiation has to be controlled (Lytle et al., 2014). However, in the last decades, an increasing trend is the reuse of the sludge by means of different alternative strategies as for agricultural purposes or as for building materials, but also in this case it is extremely important to know the radiological content of these samples to minimize the associated risks.

DWTP facilities normally collect superficial water or groundwater to produce water that is suitable for human consumption. The raw water follow a fairly standard sequence of processes, which essentially consists in solids separation using physical processes as filtration, and chemical processes such as coagulation and disinfection. As a consequence of this treatment, the different pollutants present in the raw water as radionuclides can concentrate in the sludge generated. For this reason, this industry is included in the group called as naturally occurring radioactive materials (NORM) industries.

The presence of NORM can lead to radiation doses that not are insignificant from a radiation protection point of view. For this, within the European Union, Council Directive 96/29/Euratom paid important attention to natural sources of radiation. From that moment, EU Member States are obliged to identify work activities that can involve a radiological risk and for that, most of them have implemented regulations devoted to natural sources of radiation in their own national legislations. So since 1996 the European Commission has moved ahead publishing on regular basis, technical support guidance and recommenddations on NORM issues. In this sense, in 2001 the European Commission published recommendations dealing with exemption and clearance levels for NORM residues. All these recommenddations have provided member states with criteria and a technical framework to help in the establishment of national regulations for NORM (European

Commission, 2001). In particular the clearance levels established for natural radionuclides from the ^{238}U was 1000 Bq/kg, the same activity concentration for natural radionuclides for the ^{228}Th and 10000 Bq/kg for ^{40}K. However, in order to harmonize, promote and consolidate the recommendation established in the Radiation protection 122, the European Union established in 2013 a new Council Directive laying down basic safety standards (BSS) for the protection against the danger arising from exposure to natural sources of ionising radiation, in this EU-BSS the clearance level for natural radionuclides from ^{238}U and the ^{228}Th established in 1000 Bq/kg (EURATOM BSS, 2013).

The aim of this review is to discuss from the radiological point of view, different studies focused on the characterization of the sludge generated in DWTPs, giving special emphasis on the recent studies about the new methodologies used for the determination of the main radionuclides which can be present in this kind of samples. Finally, we also point out the main strategies followed for the disposal of this sludge, and in particular we highlight the recent trend followed in its reuse and the main consequences that can be derived for that.

2. Influence of the treatment in drinking water treatment plants

As we have mentioned before in the Introduction section, DWTP facilities treat raw water to obtain water with a high quality to fulfil the legal requirements for water intended to human consumption. There are different studies focused in the determination of different radioisotopes in water samples from DWTP, in particular the ingoing (raw water) and outgoing (drinking water) water samples from this kind of plants, being the activity concentration found in the analysed samples in the levels of mBq/L (Ajayi and Owolabi, 2008; Baeza et al., 2012; de Oliveira et al., 2001; Jankovic et al., 2012; Palomo et al., 2010b; Walsh et al., 2014; Warwick and Croudace, 2013). For example, it is worth to mention the study of Palomo et al. (2010a) who focused their study in a DWTP located in the south of Catalonia (Spain) during a period of six years. In particular, the authors evaluated the capacity of this plant to remove several natural and anthropogenic radionuclides. For that purpose, first gross alpha, gross beta, residual gross beta and tritium activities were determined in the ingoing and outgoing water samples. Among all the parameters studied, gross alpha activity was the most critical because the values obtained were near to the gross alpha normative limit in Spain (0.1Bq/L)

(Spanish Government, 2003). The authors also evaluated the removal capacity of the plant and they confirm that the elimination rate was around 20% and 5% for alpha and beta emitters, respectively, and they related these results with the treatment followed in the plant that uses $FeCl_3$ as coagulant, and this favours the actinide elimination as has been previously reported (Baeza et al., 2006; Gäfvert et al., 2002). Moreover, in this study, in the sludge samples generated some gamma emitters could be quantified: natural (as for example ^{40}K or ^{214}Pb) and artificial (^{60}Co, ^{137}Cs and ^{110m}Ag), these last ones could be attributed to the presence of nuclear power plant (NPP) located upstream of the DWTP on the Ebro River. From all the results obtained for the six years monitoring period the authors concluded that sludge samples can concentrate the radioisotopes which can be present in the raw water and that the major contribution to the radioactivity in the sludge samples was from natural sources (97% of total activity) whereas the contribution of artificial radionuclides was only around 3%.

In different studies special emphasis is given to the relationship between the removal of some isotopes which can be present in the ingoing water samples of DWTP with the used treatment: for example Gäfvert et al. (2002) and Baeza et al. (2006) demonstrated that the activity due to some radionuclides from uranium and thorium decay chains which are associated with particles are removed from the water by sedimentation after the addition of an iron coagulant. As an example, Baeza et al. (2006) using a pilot plant tested the effect of four different coagulants (two iron based and two aluminium based) to remove uranium and radium from a natural water. In that study it was also found that apart of the influence of the coagulant, the removal of the different evaluated isotopes was also very sensitive to the pH value. In that sense, the authors demonstrated that the best efficiency for uranium removal was obtained in all cases at pH 6, independently of the coagulant used, and the removal for uranium was around 80% for all the tested coagulants. On the other hand, in the case of radium, the highest removal for this isotope was obtained at basic pH values, but in this case, the use of different coagulants has a different influence over the removal of radium. For the iron coagulants the removal rate for radium was around 50% whereas for aluminium coagulants it was lower with values below 30%.

More recently, Baeza et al. (2012) reported another study in which the optimum treatment conditions (iron coagulant and pH) found in their previous study using a pilot plant (Baeza et al., 2006) were evaluated for a conventional DWTP located in Extremadura (South West of Spain). The authors conclude that by changing the working conditions of the plant, the gross alpha activity was reduced from 0.155 to 0.058 Bq/L and in the case of uranium the removal was in the range 53-83%. The differences observed from this study and the previously performed with a pilot plant in which they obtain higher removal rates for uranium was justified through the greater contact time between the water and the flocs in the conventional DWTP. In the case of radium, due to the low content of this isotope in the treated groundwater, the elimination rate could not be calculated.

Huikuri and Salonen (2000) also focused in the removal capacity of uranium. In particular they focused their study in drinking water treatment plants from Finland. In this case the authors evaluated the use of commercial ion exchange filters based on strong base anions and the removal of uranium was found to be over 95% using this resin, thus demonstrating the good performance of this kind of treatment in the removal of radioisotopes. In this study, water samples of different physicochemical characteristics were analysed and for all of them the results were similar.

In recent years, membrane technology has become a valuable tool in water treatment in order to produce a drinking water with a high quality. Even that this field has not been very exploited in the removal of radionuclides, there are recent studies in the literature that are focused in testing the use of these membranes, and in particular, in the use of reverse osmosis membranes by means of pilot plants (Montaña et al., 2013b; A Nieto et al., 2013; Pérez-González et al., 2012). In these studies the authors demonstrated the benefits of these new technology in the removal of alpha and beta emitting isotopes, by measuring gross alpha and gross beta activities obtaining an average removal of around 90% in the case of alpha isotopes, whereas for gross beta the obtained results for both published papers were quite different and ranged between 35% for Nieto et. al. (2013) and 93% for Montaña et. al. (2013b).

Apart of these studies mainly focused in the removal for different natural isotopes by following different treatments, other studies evaluate the removal for artificial radionuclides. For example, Gävfert et al. (2002) evaluate the use of different coagulant reagents (iron or aluminium coagulants) to remove different natural and artificial radionuclides of uranium, thorium, plutonium, polonium, strontium and caesium, among others. They studied a DWTP located in Scania (southern part of Sweden) which collects the water from lake Bolmen. They observed in the study, that artificial radionuclides such as strontium and caesium showed lower elimination ratio than the natural radionuclides. For strontium and caesium the same activity concentration was obtained in the incoming water as in the purified water distributed, which shows that the purification processes are not effective for these radionuclides. Goossens et al. (1989) evaluated the elimination of different isotopes as caesium, ruthenium, iodine and cobalt in a drinking water treatment plant located in Brussels downstream (45 km) of a NPP. In particular, that DWTP used as coagulant aluminium hydroxide. The authors observed that the elimination rate of the studied isotopes was 73% for ruthenium, 61% for cobalt, 56% for caesium and 17% for iodine, and also they conclude that the removal increased with the turbidity.

3. Determination of radionuclides in sludge samples

It is obvious from previous sections that due to the physical-chemical processes involved in the water treatment facilities, the generated sludge trends to concentrate some of the radioisotopes which can be present in the treated water. For this, it is important to develop methods that allow the radiological characterization of these kind of samples to avoid its harmful properties.

The determination of radionuclides in environmental samples involves in some cases tedious radiochemical processes prior to the activity measurement. In particular, when sludge samples have to be analysed physical processes as drying, grinding and sieving, or also chemical processes, as the extraction of the radionuclides of interest from the sample matrix, have to be considered (Holm et al., 1984; Matthews et al., 2007; Persson and Holm, 2011; Qiao et al., 2009; Thakur and Mulholland, 2012). However, in some cases, if the final purpose is to obtain general information about the alpha and beta emitters present in the sludge, the procedure can be simplified since in this case gross alpha and gross beta activities can be easily measured. For example, in the study of Montaña et al. (2013a) these parameters were measured from different sludge samples obtained from different water treatment plants. These determinations were performed by using 0.05 g of dried sludge which was uniformly deposited onto a 20 cm^2 stainless steel planchet with 20 mL of distilled water and then they were dried at 100 ºC. Finally the measurements were done with a low level gas proportional counter. The values of gross alpha activity were between 97 and 861 Bq/kg, whereas for the gross beta values were between 172-1463 Bq/kg. The differences between the minimum and maximum values for gross alpha and gross beta activity is due to the different location and different treatment carried out in each water treatment plant. The authors observed that solid waste presenting high levels of gross alpha and beta activity also showed low values of pH. Thus under acidic conditions (pH around 5) solubility decreased and the isotopes could precipitate.

Even the important information obtained by measuring global indexes as gross alpha and gross beta, the individual determination of different radionuclides is very important in order to obtain more detailed information regarding the radiological content of these samples. Table 1 shows an overview of the different studies published in the literature regarding the individual determination of different isotopes in sludge samples from DWTP. In this table, we summarize the radionuclides determined in each study as well as the separation process followed for the isolation of the desired isotopes, and also the used techniques for their determination in the sludge samples, and as additional information we report also the activity concentration levels found.

As it can be observed from the table, we can highlight the use of gamma spectrometry as a very useful tool to have detailed information about the presence of different radionuclides in a simple measurement without the need of a previous exhaustive sample preparation procedure (Gäfvert et al., 2002; Kleinschmidt and Akber, 2008; Montaña et al., 2013a; Palomo et al., 2010b, 2010c; Puhakainen and Rahola, 1989; Walsh et al., 2014). In general for this measurement, samples are taken from mechanically dried sludge, and then after their introduction in Marinelli-beakers of about half a litter they are measured for a long period of time (usually of around 70000 seconds) to be able to determine the possible gamma emitters at the low activity levels at which they are present in this kind of samples (Baeza et al., 2006). Using this technique different natural radionuclides were detected in sludge samples from DWTP located in different places around the world such as in Sweden (Gäfvert et al., 2002), Australia (Walsh et al., 2014) and Spain (Palomo et al., 2010b, 2010c). For example, in the study of Gäfvert et al. (Gäfvert et al., 2002) the gamma emitters that showed the highest activity were ^{210}Pb and ^{7}Be with activity concentrations up to 368 and 353 Bq/kg, respectively.

Another study in which sludge samples from eleven different DWTP located in different areas of Spain were compared for their radiological content is the reported by Palomo et al. (2010b). In this case, the obtained gamma activities showed that the highest activities corresponded to ^{40}K, ^{210}Pb and ^{234}Th, with maximum activity concentrations of 4500, 1050 and 875 Bq/kg, respecttively. In the comparison between the results obtained for the different plants, the authors could conclude that in the case of the DWTP that collects water from the Ebro River in the South

Table 1. Analytical methods to determine radionuclides in sludge from different DWTPs

Country	Amount of sample	Digestion	Radionuclide	Separation process	Determination	Presence (Bq/kg)(d.w.)*	Reference
Finland	500g	-	Gamma emitters	-	Gamma spectrometry	^{103}Ru: 0-340 ^{106}Ru: 1100-4200 ^{110m}Ag: 0-230 ^{125}Sb: 0-220	(Puhakainen and Rahola, 1989)
Sweden	n.e.	n.e.	Plutonium, thorium, uranium, lead, berilium	Co-precipitation Liquid-liquid	Alpha spectrometry Gamma spectrometry	$^{239/240}$Pu: 0.72-0.86 ^{232}Th: 4.5 ^{234}U: 43-45 ^{238}U: 61-62 ^{210}Pb: 230-368 ^{7}Be: 280-353	(Gäfvert et al., 2002)
Spain	500mg	MW with HNO_3:HCl:HF (9:3:6ml)	Uranium, radium, polonium and thorium	Co-precipitation; Dowex 1x4 resin	Alpha spectrometry	^{234}U: 720-12000 ^{238}U: 660-7800 ^{226}Ra: 23-7140 ^{210}Po: 24-600 ^{228}Th: 57-870 ^{230}Th: 1.3-5.4	(Baeza et al., 2014)
Spain	250mg (alpha) 500g (gamma)	MW with HNO_3/HCl (3:1)	Uranium and thorium	Co-precipitation; Liquid-liquid extraction; AG1-resin.	Alpha spectrometry Gamma spectrometry	^{234}U: 24-790 ^{238}U: 19-590 ^{235}U: 0.3-27 ^{230}Th:8-90 ^{232}Th: 4-30 ^{40}K: 10-4600 ^{214}Bi: 20-400 ^{210}Pb: 10-1050 ^{234}Th: 10-875 ^{214}Pb: 10-405 ^{228}Ac: 10-380	(Palomo et al., 2010b)
Spain	500mg	MW with HNO_3/HCl (3:1)	Strontium and lead	LOV-MSFIA	Liquid Scintillation Counting	^{90}Sr: 34-76 ^{210}Pb: 38-63	(Mola et al., 2014)

Country	Amount of sample	Digestion	Radionuclide	Separation process	Determination	Presence (Bq/kg)(d.w.)*	Reference
Spain	100g	-	Gamma emitters	-	Gamma spectrometry	^{228}Ac: 11-73 ^{212}Pb: 7-56 ^{212}Bi: 8-66 ^{208}Tl: 1.9-16.5 ^{214}Pb: 12-132 ^{214}Bi: 11-121 ^{7}Be: 75-517 ^{40}K: 133-478 ^{137}Cs: 0.9-2.6 ^{234}Th: 39-387	(Montaña et al., 2013a)
Australia	100g	-	Gamma emitters		Gamma spectrometry	^{238}U^{238}: 30-250 ^{226}Ra: 6-120 ^{210}Pb: 10-110 ^{232}Th: 12-77 ^{40}K: 60-330 ^{7}Be: 9-480	(Kleinschmidt and Akber, 2008)
Spain	500g	-	Gamma emitters	-	Gamma spectrometry	^{228}Ac: 12-212 ^{212}Pb: 4-92 ^{212}Bi: 10-40 ^{208}Tl: 5-73 ^{214}Pb: 49-731 ^{214}Bi: 44-693 ^{7}Be: 4-293 ^{40}K: 127-1391 ^{110m}Ag: 1-76 ^{58}Co: 0.4-17 ^{60}Co:1.5-33 ^{137}Cs: 0.9-6.5 ^{54}Mn: 1-9	(Palomo et al., 2010a)

Country	Amount of sample	Digestion	Radionuclide	Separation process	Determination	Presence (Bq/kg)(d.w.)*	Reference
USA	0.5g	MW with HNO_3	Uranium, thorium and radium.	Anion Exchange resin.	Alpha spectrometry	^{226}Ra: 111-9250 ^{228}Ra: 148-12987 ^{228}Th: 22.2-2627 ^{230}Th: 7.4-360 ^{234}U: 14.8-333 ^{235}U: 37-74 ^{238}U: 11-203	(Lytle et al., 2014)
Poland	n.e.	n.e.	Radium and uranium	Coprecipitation (radium) and anion Exchange resin (uranium)	LSC (radium) alpha spectrometry (uranium)	^{226}Ra: 48-437 ^{228}Ra: 80 - 3654 ^{238}U: 15-49	(Chmielewska et al., 2014)

* d.w.= dry weigh

n.e. =not specified

South of Catalonia, higher activities for ^{214}Bi and ^{214}Pb (405 and 410 Bq/kg, respectively) were obtained than for the other plants, and this situation could be attributed to different reasons, the first one was the presence of a DCP factory upstream of the river and the second one was due to the different procedure followed in the water treatment since in this case they used as coagulant $FeCl_3$ whereas in the rest of the evaluated plants they used an aluminium coagulant. Moreover, for this water treatment plant (in the Ebro River) the same research group could determine the presence of different artificial radionuclides in the analysed sludge samples (Palomo et al., 2010b). Although the low activity concentration showed by the artificial radionuclides in these samples, the measurement time of 20 hours was enough to quantify them. Among the different isotopes found we can highlight ^{110m}Ag, ^{60}Co, ^{58}Co and ^{137}Cs, which presence could be attributed to the presence of a Nuclear Power Plant upstream of the PWTP, however, it is important to remark that the concentration activities found for these radionuclides were very low (up to 76 Bq/kg) in comparison to the activities for the natural radionuclides. In the study reported by Puhakainen and Rahola (1989), sludge samples from a DWTP located near to Loviisa and Olkiluoto NPPs in Finland were analysed. In particular, the authors could quantify in the sludge samples different gamma emitting radionuclides as ^{103}Ru, ^{106}Ru, ^{110m}Ag and ^{125}Sb, with activity concentrations of 4200 Bq/kg for ruthenium and between 220 to 340 for the rest. Even these differences, not specific information is given in the manuscript to justify them.

There are also some studies in which some alpha or beta emitting radionuclides have been determined in sludge samples from DWTP (Baeza et al., 2014; Gäfvert et al., 2002; Lytle et al., 2014; Mola et al., 2014; Palomo et al., 2010c). For that purpose, normally most time-consuming methods are required thus involving more steps in the pretreatment of the sample in order to isolate the radionuclide of interest. In Figure 1, a basic scheme of a general procedure to determine alpha and beta radionuclides in the sludge samples is shown. Most of the methods could be divided in different steps such as the pretreatment of the sample, the digestion, the separation of the radionuclide from the interferences and finally the radioactivity measurement.

From the literature it can be drawn that the first step in the different methods for determining α and β emitting radionuclides consists in the digestion of the sample. Chemical preparation involves dissolution of the sample itself and the destruction of organic matter. There are three different digestion methods that have been traditionally used: classical wet ashing with acids in

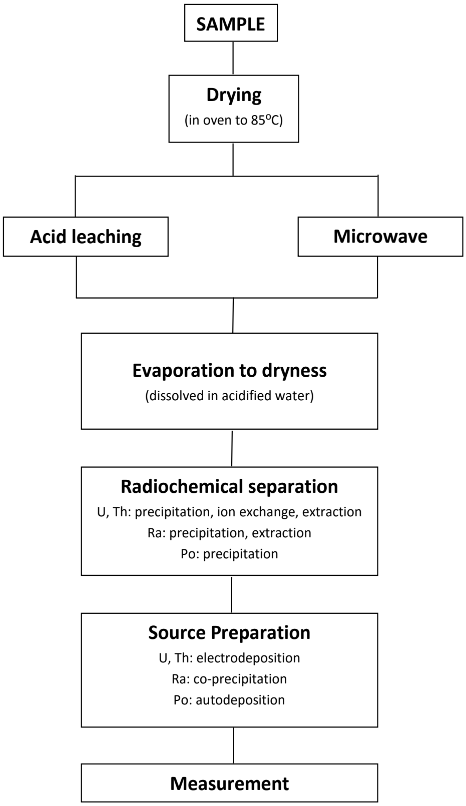

Fig 1. Basic scheme of methodologies to determine alpha and beta emitters in sludge samples

a 100 mL long-necked quartz kjeldahl flask by heating vigorously over a gas flame, open digestion with acids in an Erlenmeyer flask at a temperature on a hot plate up to 200 ºC, and wet digestion by a microwave system in a Teflon vessel up to 200 ºC (Matthews et al., 2007; Mola et al., 2012; Sanchez-Cabeza et al., 1998). The classical method has some disadvantages such as time-consuming steps, risk of external sample contamination and formation of insoluble salts during sample evaporation. In the case of an open acid digestion method high temperatures (140-160 ºC) and long periods of time, between 2-12h, are usually required. The microwave acid digestion could be regarded as the birth of an effective method for the preparation of solid samples. It assures a complete digestion of the material, the analysis time is reduced, and contamination and health risks are minimized, and moreover better reproducibility is usually obtained (Montaña et al., 2013a). Regarding the use of this last strategy, and as it can be seen in Table 1, the most used acids have been HCl, HNO_3, HF, H_3PO_4 in different proportions and in some cases, it is used some drops of H_2O_2 to facilitate organic matter dissolution (Baeza et al., 2014; Mola et al., 2014; Palomo et al., 2010c). These acids were chosen because they are commonly used in the conventional acid leaching method. As example, the study of Mola et al. (2012) compared two digestion methods (the open digestion and the microwave digestion using in both cases HNO_3:HCl (3:1)) followed by a separation using chromatographic resins and the alpha spectrometry detection to determine uranium and thorium in sludge samples. They obtained some advantages using the microwave digestion such a few amount of sample required and higher recoveries for thorium were obtained.

The recoveries for thorium were 61% using the open acidic digestion, whereas using the microwave digestion the recovery increased until 82%.

After the digestion of the sample, the next step consists in the individual separation of each radionuclide and for that the usual strategies are solvent extraction (Baeza et al., 2014; Palomo et al., 2010c) and extraction chromatography (Lytle et al., 2014; Mola et al., 2014). For example, in the study of Baeza et al. (2014) the presence uranium, radium, thorium and polonium were determined using a solvent extraction methodology. After a co-precipitation method with $Fe(OH)_3$, the precipitate was redisolved with HNO_3 acid and then a liquid-liquid extraction using tributyl phosphate (TBP) as organic solvent was done, in this step the aqueous phase was discharged. Next, they added a mixture of xylene and HCl 1.5M and the aqueous fraction which contained thorium and impurities was separated. To separate uranium they took the organic phase and added water and uranium was retained in the aqueous phase. Then the solution with thorium isotopes and impurities was passed through a column which contained BIORAD AG1-X8 Resin to remove impurities. Finally the solution was transferred to an electrodeposition cell and submitted to electrolysis on stainless steel planchets to determine the uranium and thorium radionuclides using the alpha spectrometry detection. They studied the presence of ^{234}U, ^{238}U, ^{226}Ra and ^{228}Th in four different DWTP which collect water from groundwater or surface water. The highest activities found were 7000, 1260, 6340 and 870 Bq/kg for ^{234}U, ^{238}U, ^{226}Ra and ^{228}Th, respectively. As it is already known the clearance level in the new EU-BSS is 1000 Bq/kg for the ^{238}U and ^{232} Th series and in all DWTPs there at least one radionuclide that showed higher values than the clearance levels.

Palomo et al. (2010b) using the same extraction method obtained an average yield of 49 and 46% for thorium and uranium, respectively. In their study they measured the presence of ^{234}U, ^{235}U, ^{238}U, ^{230}Th and ^{232}Th, and they observed the highest activities of uranium in the DWTPs located in the North of Catalonia. This is an area in which granite predominates and the concentrations found were 730 and 590 Bq/kg of ^{234}U and ^{238}U, respectively. Therefore, the relative high activities found for uranium may be correlated with the geology of the area. Regarding the thorium activities were lower than the activities of uranium, and the highest concentrations were 90 and 30 Bq/kg for ^{230}Th and ^{232}Th, respectively.

Nowadays, one of the trends in the separation of radionuclides is the use of chromatographic resins due to their versatility and the advantages in front of the traditional techniques such as liquid-liquid extraction (Lytle et al., 2014; Mola et al., 2014). There are available different commercial materials which are specific for different radionuclides such as Sr-Spec for strontium, UTEVA resin for the transuranium tetravalent radionuclides, TRU for ^{55}Fe and Ni-resin for ^{63}Ni, among others. For example, Mola et al. (2014) developed an automatic method based on the use of lab-on-valve and multisyringe flow injection analysis (LOV-MSFIA) to separate ^{90}Sr and ^{210}Pb. The authors used a Sr-Spec resin with the aim to determine these radionuclides in sludge samples from a PWTP located in the South of Catalonia (Spain). The use of this automatic method gives the authors different advantages such as less time consuming and environmentally friendly. After the microwave digestion of the sample, it was redissolved in HNO_3 2M. Once the sample was passed through the column, using different acidic conditions and different solvent combinations the separation of both radionuclides was done. Finally, the detection of both radionuclides was performed using a liquid scintillation counter and the analysis time was 500 min. Under optimal conditions, recoveries of 90% and 98% for Sr and Pb, respectively, were obtained. The authors demonstrated that the method used has shown to be a good alternative to manual radiochemical separations, determining both radionuclides with simple equipment, reduced consumption reagents, minimal production of effluents and minimal resin used. In the samples analysed from a DWTP located in Spain, the authors determined concentrations up to 66 and 63 Bq/kg for ^{90}Sr and ^{210}Pb, respectively. Lytle et al. (2014) also reported an study in which they used a resin. In particular, they performed their study using an anionic exchange resin, Biorad AG1-X4, to separate uranium and thorium isotopes from sludge samples. Prior the separation the samples were digested using a microwave digestor. For the uranium separation the digested samples were directly passed through the column with the resin whereas, for the thorium determination the digested samples were precipitated in the presence of potassium sulphate to form thorium sulphate, which was dissolved in alkaline EDTA and precipitated as thorium hydroxide. After that the precipitate was dissolved in nitric acid and pass through the resin. In both cases, for uranium and thorium, after the separation the samples were determined by alpha-particle spectrometry. The authors found that thorium was the second most abundant radionuclide in the solid samples analysed after radium. Total thorium (^{228}Th, ^{230}Th and ^{232}Th) levels ranged between 0.04 and 3.7 Bq/g, being ^{228}Th the isotope that showed the highest contribution. In the case of uranium the activity concentrations were lower with values ranging between 0.03 and 0,63 Bq/g for total uranium (^{234}U, ^{235}U, ^{236}U and ^{238}U) levels ranged. In the case of ^{210}Po determination, the used methodology is rather simple since in this case, after the microwave digestion, the sample was evaporated until dryness at temperature below 100 ºC and redissolved in HCl media. In the determination of this radionuclide is important that the temperature does not exceed 100 ºC because ^{210}Po is not stable at high temperatures. Then it was autodeposited onto silver planchets, and measured by alpha spectrometry (Baeza et al., 2014; Matthews et al., 2007; Sanchez-Cabeza et al., 1998). The mean value of the recoveries in these studies was around 51% for 210Po. Baeza et al. (2014) evaluated the presence of polonium in three different DWTPs which treated groundwater. They observed that depending on the water treated the activity of polonium could vary between 24 and 600 Bq/kg.

Another isotope that should be considered for its intrinsic risks in these sludge samples from DWTP is ^{222}Rn . Although in the literature there are not specific data available about its presence in this kind of samples, it is important to take into account this isotope due to its potential exposure risk for the workers in the DWTP, because due to the presence of isotopes of uranium and radium, the radon could emanate from the sludge and accumulate in closed places. Radon activity concentration in indoor air of waterworks depends on many factors, such as the ventilation and type of water input (Chmielewska et al., 2014; Michael et al., 2014; Vaupotic, 2002). All the studies about the determination of 222Rn in DWTP are focused on the total effective dose received by the workers. In general all the DWTP studied, showed a total effective dose from radon inhalation were below 1 mSv/year (EURATOM BSS, 2013). In this sense, it is important to highlight that the accumulation of radon may cause radiologic hazards for the water treatment plant operators such as lung cancer (Nasir et al., 2014).

4. Reuse of sludge

The sludge removed from DWTP generates amounts of waste and this should be properly managed. According to environmental protection regulations, sludge that is produced within the production of drinking water is a solid residue that should be properly treated and disposed in a way which does not adversely impact human health and the environment (IAEA, 2003b). In general, water treatment plants have different disposal alternatives for the generated sludge being the most acceptable practice the long-term disposal method landfilling. However, this is becoming increasingly difficult due to the large volumes produced and the limited available land for disposal, and for that other options should be considered. In this sense, in last years some efforts have been directed towards the reduction of the volume of this produced sludge and in this way the associated handling and transport costs during sludge disposal can be minimized. Moreover, the reuse of this sludge for different applications as for the cement industry or also for agricultural purposes is a practice that in recent years is increasingly considered (Caniani et al., 2013; Kyncl, 2008; Teixeira et al., 2011).

In most of cases, before the possible reuse of the sludge generated in a DWTP, the first step is a partial dehydration, resulting in a cake with a concentration of solids of 60 to 70%. This cake can be used as fertilizer, incinerated, disposed in landfills for urban waste, and composted with urban waste, among other alternatives (Baeza et al., 2014). Recently, different options in which the residue is used or transformed into products that are useful to society have been studied, and in this regard its use in cement and ceramic bricks production has been evaluated although in them the radiological aspects were not evaluated (Husillos Rodríguez et al., 2010; Torres et al., 2012).

However, one should consider the potential hazards of these strategies, since for example when sludge is used to produce cement, one of the most important parameters from the radiological point of view, is the radon exhalation (Nasir et al., 2014). In the new EU-BSS, the parts are dealing with radon issues, fixing a maximum national reference level for all buildings, at 300 Bq/m3 in the BSS article 74.1 (EURATOM BSS, 2013). The presence of radon in the sludge might be attributed to the atmospheric deposition and due to the concentration of the natural radionuclides during the conventional treatment process in the DWTPs (Kleinschmidt and Akber, 2008).

In the literature there are also studies in which sludge has been used to remove phosphorus from soils (Verlicchi and Masotti, 2012). This can be related to the presence of aluminium and iron hydroxides (flocculants used for its precipitation in the process) in the sludge, and these compounds can favour the fixation of available phosphorus (PO_4^{3-}). This can be positive if the soil is subjected to an excessive phosphorous load for example to the spreading of farm organic wastes. In addition to removing phosphorous from soils, sludge has the proven ability to absorb and remove other anions from the environment such as perchlorate arsenic and selenium (Ippolito et al., 2011). Furthermore, sludge used in agriculture requires an evaluation of the effects on soils physical properties (cohesion, aggregation, strength and texture which affect hydraulic properties of the soil), on plant growth and on groundwater quality. In this point, is important the study of the transference of radionuclides between the sludge used in the agriculture and plants (Willey, 2014). In this sense, an analytical protocol is designed to test the suitability of the sludge produced by the drinking water treatment plant, mixed with municipal solid waste stabilized organic fraction, SOF, in order to create innovative "bio-soils" to be used for daily and final covering in controlled landfills (Caniani et al., 2013). Another possible reuse of the sludge generated in the DWTP is the introduction of sludge in different zones which are affected by the coastal erosion. In this sense, in 2013, a new Life Project entitled "Adaptation and mitigation measures to climate change in the Ebro Delta" organized by Research and Technology Food and Agriculture Institute from Catalonia (IRTA) in collaboration with different organisms is evaluating the possibility of introducing the sludge generated in the DWTP of L'Ampolla (Tarragona, Spain) in the Ebro Delta to restore the sediment flow by increasing sediment deposits in the delta (Life Ebro-Admiclim, 2013). in this regard, In order to assure the convenient management of the sludge samples is important an exhaustive characterization of different chemical and physical parameters and among them the radioactive content should be considered.

5. Conclusions

Although the treatments carried out in the DWTP achieve a partial or a total removal of the radionuclides from the raw water, and consequently the water produced is suitable for the human consumption, their normal operation also produced a concentration of the radionuclides in the sludge generated.

The most abundant radionuclides in the sludge are natural radionuclides such as uranium, thorium, radium, lead and polonium, among others with activity concentrations ranging from 10 to 7000 Bq/kg. The concentration of these radionuclides depends on the characteristics of the raw water used in the DWTP and also on the treatment followed in the plant.

To date most of the sludge produced during water treatment has been used in agriculture or disposed in landfills and also in some cases it has been used for building materials. However, the possible presence of both man-made and natural occurring radionuclides in this kind of samples should be considered before its reuse since a potential radiological hazard should be derived from that, so the reuse routes can be considered insecure in some cases. So in this regard, more investigation is needed to explore novel trends in sludge handling since until now sludge has been disposed or reused without any or limited specific control and this can be a problem in some cases due to its radiological content.

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1.3 El Delta de l'Ebre: cultiu de bivalves

El riu a la part baixa es divideix en dos hemideltes. L'hemidelta dret ocupa una extensió de 186.46 Km^2 incloent la Punta de la Banya i la Barra del Trabucador, amb una extensió de 25 Km^2 (delimiten la Badia dels Alfacs). D'altra banda, l'hemidelta esquerre ocupa una extensió de 119.22 Km^2 incloent la punta del Fangar (4.1 Km^2) que delimita la Badia del Fangar. De la mateixa forma que hi ha dos hemideltes, també existeixen dos canals de regadiu, el canal de la dreta i el de l'esquerra (segons la seva situació respecte al riu), els quals tenen origen a 60 km de la desembocadura. Aquests canals corren de forma paral·lela al riu, dividint-se en altres canals secundaris que són els encarregats de regar els camps (Figura 1.9). Aquells canals que recullen l'aigua de les plantacions i porten l'aigua a la badia, són els canals de desguàs. Així doncs, les aportacions a les badies són: a) aigua dolça procedent del riu Ebre, b) aigua dolça procedent de petites planures litorals i c) una aportació dolça procedent de l'aigua freàtica present al delta.

Finalment, a la desembocadura del riu Ebre es forma el delta de l'Ebre degut a les aportacions al·luvials del riu Ebre damunt una extensa plataforma submarina. Té una extensió d'uns 320 km^2 (220 km^2 de terra consolidada i 100 més entre aiguamolls, basses i illes) i una penetració, Mediterrània endins, d'uns 25 km^2.

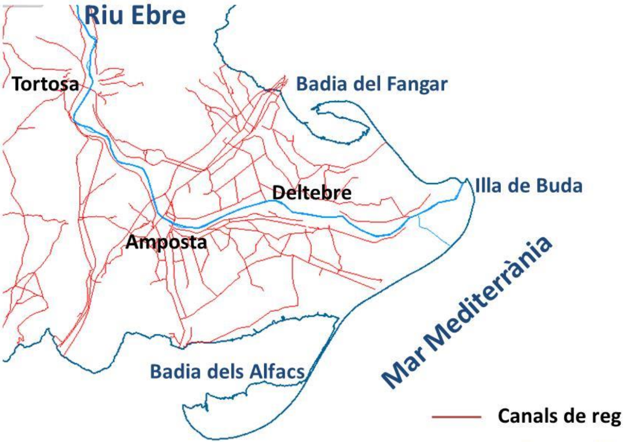

Figura 1.9 Mapa de la zona deltaica de l'Ebre.

Així doncs, les aigües de la costa són riques en nutrients, i alimenten la gran concentració d'algues planctòniques que són la base de la cadena tròfica de les dues badies [84]. Aquestes condicions s’aprofiten per conrear bivalves (principalment: musclos, ostrons i cloïsses). La producció global de les empreses agrupades en la Federació de Productors de Mol·luscs del delta de l'Ebre (Fepromodel) és de 4.000 tones de musclo, 800 tones d'ostró i 30 tones de cloïssa. Aquesta zona es considera la zona més important de producció de marisc del Mediterrani espanyol [85]. A la Figura 1.10 podem veure l’àrea del delta de l’Ebre on es cultiven bivalves, així com també una ampliació de les cordes d’ostró i la collita de musclos.

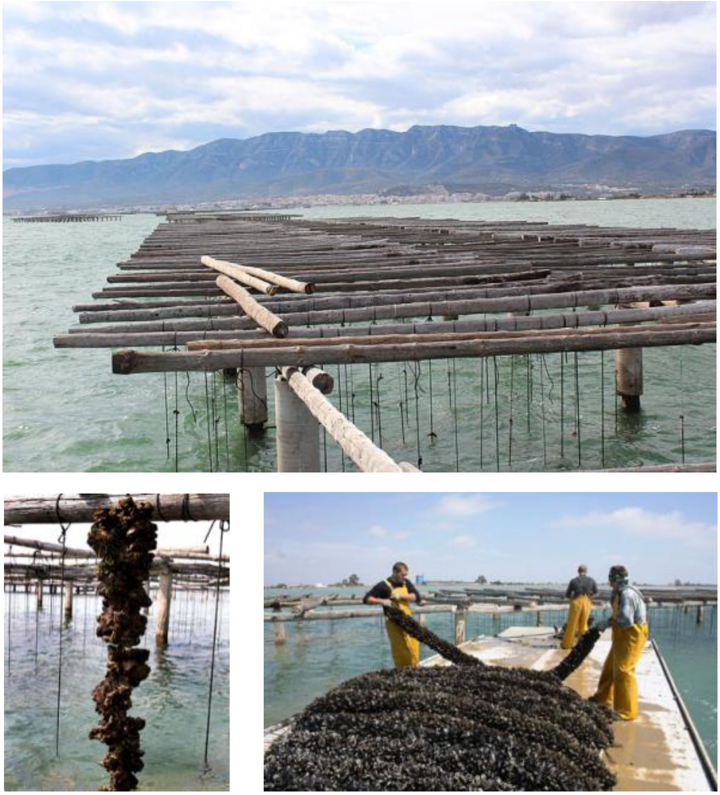

Figura 1.10. Cultiu de bivalves a la badia del fangar. Dalt: bats de musclos, baix esquerra: corda d’ostró, baix dreta: collita del musclos.

Els bivalves són organismes que filtren aproximadament 80 L d’aigua al dia en condicions òptimes (temperatura de l’aigua, disponibilitat alimentària, cicle de reproducció) [86]. A més de ser filtradors, també són consumidors de fitoplàncton i tenen alta capacitat de retenció de partícules amb alt grau d’associació de radionúclids.

És per això que aquests organismes s'han considerat bioindicadors ideals de la contaminació radioactiva [86–89].

Des del punt de vista radiològic, hi ha diversos estudis a la bibliografia centrats en aquests tipus de mostres. En tots, els radionúclids més analitzats són el ^{210}Po i el ^{210}Pb, donat que aquests radionúclids entren al medi marí i a l'aigua a través de la precipitació d'aerosols, gasos, de l'alliberament de material de l'escorça terrestre i finalment a través de sub-productes alliberats d'indústries principalment NORM [90]. A més a més, el ^{210}Po es considera un dels isòtops més tòxics i un dels majors contribuïdors de la dosi de radiació interna rebuda pels humans degut al seva amplia distribució i l'alt potencial d'exposició a través de la ingesta i la inhalació [91–93].

Pel que fa a la conca del riu Ebre, només hi ha un estudi realitzat per Nadal i col. [94] centrat en la determinació de ^{210}Po, ^{210}Pb, alfa total i beta total en diversos grups de menjar (l'arròs, peix, marisc, vegetals i fruites) potencialment influenciats per la presència de sediments d'elevades concentracions d'activitat d'^{238}U a l'embassament de Flix. D'aquest estudi, cal destacar que dintre del grup de bivalves es van analitzar musclos i cloïsses, sent els aliments amb les activitats més elevades de ^{210}Po (valors de 237 ± 178 i 170 ± 361 Bq/kg, respectivament). Tot i això, els autors conclouen que l'exposició a aquests radioisòtops no constitueix un risc addicional per a la població que viu a l'àrea afectada.

Tot i la limitació d'aquests estudis a la conca del riu Ebre, hi ha molts estudis a nivell internacional basats en la distribució de ^{210}Po i ^{210}Pb en diferents ecosistemes. Així doncs, per tal de realitzar una comparativa es presenten els resultats obtinguts als diferents estudis a la Taula 1.3.

D'aquest recull d'estudis es pot destacar que les zones amb indústries NORM (com és la central tèrmica de carbó, indústries de processat de metalls, indústries de paper, etc.) presenten altes concentracions d'activitat de ^{210}Po en els bivalves analitzats [92,95,96]. Un exemple és l'estudi de Rozmaric i col. [95] on hi ha una certa influència antropogènica i a més a més, descàrregues d'aigües subterrànies. Les concentracions d'activitat trobades varien entre 118.24 i 1053.63 Bq/kg pel que fa a l'anàlisi de ^{210}Po en musclos. Similarment passa amb els estudis de Aközcan i Aközcan i Ugur [92,96], en els que s'analitzen musclos en zones amb influència d'indústries NORM. Els valors de concentració d'activitat de ^{210}Po són 332 – 776 i 34 – 1855 Bq/kg, respectivament. D'altra banda, hi ha d'altres estudis que no especifiquen l'activitat industrial de la zona o només remarquen el seu interès en veure el fons radioactiu de la zona [97–99], les activitats en aquests casos són força més baixes, d'entre 10 i 390 Bq/Kg. I finalment, en zones sense afectació d'indústries NORM s'han trobat valors de ^{210}Po en els mol·luscs analitzats (4.5 i 54.4 Bq/kg) [100].

Tot i que el radionúclid amb més interès és el ^{210}Po, el seu progenitor, el ^{210}Pb amb una vida mitja de 22.2 anys, també ens dóna informació rellevant. Diversos estudis, ressalten l'interès d'analitzar el ^{210}Pb per veure la procedència del ^{210}Po [92,101]. En l'estudi d'Aközcan [92], s'atribueixen les diferències d'activitat entre el ^{210}Po i el ^{210}Pb a que el ^{210}Po obtingut no és totalment procedent del decaïment del ^{210}Pb, per tant és d'origen antropogènic. En canvi, en l'estudi de Khan i Godwin Wesley [100] s'atribueixen les diferències de les concentracions d'activitat obtingudes a que la majoria del ^{210}Po s'acumula selectivament en relació al seu precursor. En els diferents estudis de la bibliografia no es pot veure una clara relació entre els valors d'activitat d'aquest radionúclid i el tipus d'afectació industrial, tot i així els valors de ^{210}Pb solen ser força més baixos que els de ^{210}Po en les zones sense afectació d'indústries NORM. En el cas del musclo, els valors d'activitat de ^{210}Pb en àrees sense afectació NORM són de 4.9 ± 2.4 Bq/Kg [100], en canvi en zones amb afectació industrial NORM, varien entre 4.5 ± 6.0 i 64 ± 6 Bq/Kg [90,92,94–96].

Finalment, cal destacar un treball recent realitzat per Bode i col. [99] on s'estudien els factors que afecten a les activitats de ^{210}Po dels musclos degut a que hi ha molts estudis on s'ha demostrat que els canvis estacionals poden afectar a les concentracions d'activitat dels musclos. Els autors conclouen que les concentracions d'activitat de ^{210}Po són més elevades durant les estacions més fredes de l'any i majoritàriament ho atribueixen a dos factors: el cicle biològic i les condicions ambientals. Pel que fa a les condicions ambientals, les concentracions d'activitat màximes de fitoplàncton mostren valors màxims de ^{210}Po, així com també veuen una forta relació amb la quantitat de matèria particulada procedent d'aportacions d'aigua superficial.

Taula 1.3. Comparativa de les activitats trobades (Bq/Kg pes sec) en relació amb l'activitat industrial de cadascuna de les diferents zones. (n.e = no especificat).

Lloc	Tipus de mostres	Tipus d'afectació industrial	^{210}Po	^{210}Pb	Referències
Voltants del riu Ebre (Espanya)	Musclos	Indústria NORM (fosfat bicàlcic)	237 ± 178	4.5 ± 6.0	[94]
	Cloïsses		170 ± 361	2.5 ± 2.7	
Costa oest de Portugal	Musclo	n.e	132 ± 5	2.6 ± 0.1	[97]
	Cloïssa		152 ± 19	2.9 ± 0.1	
	Ostró		10 ± 1	0.5 ± 0.07	
Costa de Kudankulam (Índia)	Gastròpodes	Instal·lació nuclear	4.5 - 8.9	16.8 - 38.6	[100]
	Musclo marró		54.7 ± 4.7	4.9 ± 2.4	
Costa de Point Calimere (Índia)	Cloïsses	Àrea amb un fons força radioactiu	305.4 - 596.6	6.5 - 12.9	[99]
Ennore Creek (Índia)	Musclo	n.e (línia base)	96.12 - 113.32	25.42 - 96.80	[98]
Albània	Musclo	n.e	390 ± 17 (estiu) 227 ± 5 (tardor)	-	[91]
Costa adriàtica (Croàcia)	Musclo	Descàrrega d'aigua subterrània i influència antropogènica	118.24 - 1053.63	14.98 - 38.18	[95]
Eslovènia	Musclo	Àrea afectada per antigues activitats d'extracció i processat d'urani	256.0 (estiu) 531.0 (tardor)	15.5 (estiu) 13.6 (tardor)	[90]
	Ostró		283.7 (estiu) 623.0 (tardor)	6.05 (estiu) 5.5 (tardor)	
Baia Didim (Turquia)	Musclo	Indústries: Processat de menjar, embotellat de beguda, indústries tèxtils, oli, producció de sabó i pintura, processat de metall i fusta, indústries de paper i indústries químiques	34 ± 9 - 1855 ± 98	ND - 64 ± 6	[96]
Baia Izmir (Turquia)		Central tèrmica de carbó			
Golf Candarli (Turquia)	Musclo	Industries de ferro i acer, fertilitzants, emmagatzematge de combustible i planta d'energia de gas natural	332 ± 17 - 776 ± 23	14 ± 1 - 40 ± 5	[92]

1.4 Dosi efectiva

En aquesta tesi doctoral ens hem centrat majoritàriament en determinar les activitats de diferents radionúclids en diferents tipus de mostres tant ambientals com biològiques. Tot i això, algunes d'aquestes mostres poden ser ingerides (aigües i mol·luscs) pels éssers humans a través de la seva dieta habitual.

Així doncs, quan ingerim aliments o begudes també ingerim radionúclids, destacant l'urani i els seus descendents. Per exemple, algunes aigües minerals procedents de massissos granítics rics en urani són especialment riques en material radioactiu natural. A més a més, certs aliments com el marisc també poden tenir material radioactiu donat que els radionúclids poden entrar al medi aquàtic en forma catiònica adherits al material particulat. Un cop a l'aigua, pot ser absorbit per la biomassa de plàncton dels primers metres de la columna d'aigua. El fitoplàncton i el zooplàncton són l'aliment de moltes de les espècies marines, per tant, alguns dels organismes marins bioacumularan els radionúclids, fet que pot produir efectes tòxics [102].

D'acord amb el document *Safety Report Series nº 19* [103] les dosis individuals es calculen per la transferència de cadascun dels radionúclids a través dels diferents camins d'exposició. La dosi efectiva total vindrà donada per la suma de les dosis degudes a cada radionúclid i per via d'exposició, segons l'expressió:

$$D_a = \Sigma U_{a,p} \times C_{i,p} \times FCD_{a,i,p}$$

On:

D_a és la dosi efectiva anual a l'individu del grup d'edat (adult) [mSv/any], U és un paràmetre d'utilització (consum d'aliment, temps d'exposició,…) de la via d'exposició (p) per al grup d'edat (a) [m^3/any, Kg/any, s/any], $C_{i,p}$ és la concentració del radionúclid (i) a la via d'exposició (p) [Bq/m^3, Bq/Kg, Bq/m^2] i $FCD_{a,i,p}$ és el factor de conversió a dosis efectiva per a cada grup d'edat (a), radionúclid (i) i vía (p) [mSv/Bq i mSv m^3 / (Bq·s)].

En l'aplicació a aigües, el valor de $U_{a,p}$ ha estat de 2 L/dia (valor representatiu de la ingestió diària d'aigua per persona), mentre que els altres aliments s'han basat amb les dades estadístiques facilitades per Ministeri de sanitat, política social i igualtat, reflexats a la Taula 1.4 [104]. En aquest cas, l'activitat de les mostres s'ha de passar a Bq/kg pes fresc. Els valors de $FCD_{a,i,p}$ per als diversos radionúclids no són dependents del tipus de mostra amb el que s'ingereix el radionúclid sota estudi. Aquests valors es mostren a la Taula 1.5, els quals són el resultat d'un consens internacional aconseguit sota el pronòstic de l'Organisme Internacional d'Energia Atòmica (OIEA), després de l'anàlisi i avaluació de nombrosos estudis experimentals i de modelització sobre el comportament metabòlic i distribució entre òrgans dels radionúclids analitzats, un cop ingerits. Cal destacar que els factors de conversió $FCD_{a,i,p}$ són dependents de l'edat de l'ésser humà ingestor i del radionúclid sota estudi. Per una mateixa activitat de radionúclids ingerit, en general la dosi efectiva es més elevada per als lactants i la població d'edat jove en creixement, que per als adults. També cal destacar, que de tots els radionúclids mostrats a la Taula 1.5, els que presenten valors majors de $FCD_{a,i,p}$ són els radionúclids de ^{210}Po i ^{210}Pb.

Cal destacar, que en aquesta estimació, s'ha considerat el pitjor dels casos, és a dir, que tota la concentració d'activitat que conté l'aliment, s'absorbeixi per l'organisme.

Taula. 1.4. Consum dels diferents aliments estudiats, sòlids en g/persona/dia.

Producte	**Mitjana (g/persona/dia)**	**Mitjana (Kg/persona/any)**
Cloïssa	1.74	0.64
Musclo	3.15	1.15
Navalles	0.10	0.037
Ostres	0.04	0.015
Cargols de mar	0.47	0.17

Taula 1.5. Factor de conversió a dosis efectiva per a cada grup d'edat i radionúclid.

Radionúclid	Període de semidesintegració	Edat (anys)					
		<1	**1-2**	**2-7**	**7-12**	**12-17**	**>17**
Pb-210	22,3 anys	$8.4 \cdot 10^{-6}$	$3.6 \cdot 10^{-6}$	$2.2 \cdot 10^{-6}$	$1.9 \cdot 10^{-6}$	$1.9 \cdot 10^{-6}$	$6.9 \cdot 10^{-6}$
Po-210	138 dies	$2.6 \cdot 10^{-5}$	$8.8 \cdot 10^{-6}$	$4.4 \cdot 10^{-6}$	$2.6 \cdot 10^{-6}$	$1.6 \cdot 10^{-6}$	$1.2 \cdot 10^{-6}$
Ra-226	$1.6 \cdot 10^{3}$ anys	$4.7 \cdot 10^{-6}$	$9.6 \cdot 10^{-7}$	$6.2 \cdot 10^{-7}$	$8.0 \cdot 10^{-7}$	$1.5 \cdot 10^{-6}$	$2.8 \cdot 10^{-7}$
Rn-222	3.82 dies	-	-	-	-	-	$1 \cdot 10^{-8}$
Th-230	$7.7 \cdot 10^{4}$ anys	$4.1 \cdot 10^{-6}$	$4.1 \cdot 10^{-7}$	$3.1 \cdot 10^{-7}$	$2.4 \cdot 10^{-7}$	$2.2 \cdot 10^{-7}$	$2.1 \cdot 10^{-7}$
Th-232	$1.4 \cdot 10^{10}$ anys	$4.6 \cdot 10^{-6}$	$4.5 \cdot 10^{-7}$	$3.5 \cdot 10^{-7}$	$2.9 \cdot 10^{-7}$	$2.5 \cdot 10^{-7}$	$2.3 \cdot 10^{-7}$
U-234	$2.44 \cdot 10^{5}$ anys	$3.7 \cdot 10^{-7}$	$1.3 \cdot 10^{-7}$	$8.8 \cdot 10^{-8}$	$7.4 \cdot 10^{-8}$	$7.4 \cdot 10^{-8}$	$4.9 \cdot 10^{-8}$
U-238	$4.47 \cdot 10^{9}$ anys	$3.4 \cdot 10^{-7}$	$1.2 \cdot 10^{-7}$	$8.0 \cdot 10^{-8}$	$6.8 \cdot 10^{-8}$	$6.7 \cdot 10^{-8}$	$4.5 \cdot 10^{-8}$

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Capítol 2

OBJECTIUS

L'objectiu principal d'aquesta tesi doctoral és determinar diferents radionúclids tant d'origen natural (^{210}Po i ^{222}Rn) com artificial (^{55}Fe i ^{63}Ni) de manera individualitzada en diferents mostres ambientals de l'entorn del riu Ebre. Amb els resultats, es farà una avaluació de l'impacte radiològic ambiental causat per la industrialització al tram baix del riu Ebre.

També és un objectiu d'aquesta Tesi Doctoral l'avaluació de les concentracions d'activitat dels radionúclids naturals en diferents tipus de mol·luscs (musclos, cloïsses, ostres, navalles i cargols de mar) que es cultiven a la desembocadura del riu Ebre (delta de l'Ebre) per tal de fer una estimació de dosi per ingesta d'aquests aliments.

Capítol 3

PART EXPERIMENTAL I DISCUSSIÓ

En aquest capítol es mostren els resultats més rellevants dels diferents estudis realitzats en aquesta tesi. Aquests, estan publicats, acceptats o pendents de publicació en diferents revistes científiques, per aquest motiu els presentem en format d'article. La part experimental està dividida en dos blocs, prèviament a cada bloc s'inclou una breu introducció on es detallen els principals objectius i al final del bloc es presenta una breu discussió general dels resultats obtinguts.

En les dues tesis doctorals realitzades al nostre grup de recerca centrades en el desenvolupament de mètodes per a l'avaluació de la radioactivitat ambiental en l'últim tram de la conca del riu Ebre al seu pas per la província de Tarragona, es va veure una elevada activitat en una zona concreta del riu Ebre (Flix) [1,2]. En aquesta zona, hi ha una planta de fosfat bicàlcic, una de les indústries classificades dintre del registre d'indústries NORM (*Naturally Occurring Radioactive Material).* A més a més, en aquesta mateixa zona, també hi ha una central nuclear (central nuclear d'Ascó) que té dos reactors, Ascó I i Ascó II.

En el primer bloc d'aquest estudi s'ha realitzat la determinació de diferents radionúclids (naturals i artificials) procedents de la industrialització al tram baix del riu Ebre en diferents tipus de mostres procedents d'una planta de tractament d'aigua potable (ETAP). Aquesta planta, situada a uns quilòmetres sota de la zona esmentada anteriorment, es pot veure afectada de manera secundària pels abocaments de les diferents indústries al riu, donat que utilitza l'aigua del riu com a matèria primera.

En aquesta planta s'han realitzat prèviament diversos estudis per tal d'avaluar la concentració dels isòtops d'urani i tori en els fangs produïts [3,4]. Amb l'objectiu de complementar la informació radiològica, en el primer estudi realitzat s'han caracteritzat dos radionúclids emissors beta artificials (^{55}Fe i ^{63}Ni) en els fangs de l'ETAP, així com també s'ha estimat la presència d'aquests isòtops a l'aigua superficial d'entrada a la planta. Per tal de dur a terme aquest estudi, tot i haver diferents mètodes per a la separació, s'ha optat per l'ús d'una reïna d'intercanvi aniònic per a separar el ferro, i en el cas del níquel s'ha purificat amb una reïna de dimetilglioxima (DMG) a pH 8-9 [5,6], amb una posterior detecció amb un detector escintil·lació líquida.

Seguint amb la temàtica de la caracterització radiològica dels fangs de l'ETAP, es va plantejar un altre treball per determinar un dels radionúclids naturals més tòxic (^{210}Po). En aquest cas, es van provar diferents estratègies per tal d'obtenir aquest radionúclid lliure d'interferències, prèviament a la seva mesura. Les estratègies esmentades, inclouen l'estudi de diversos tipus de digestió i condicions d'auto-deposició (concentració de la solució, temperatura i temps) [7–10]. Donat que el ^{210}Po és un radionúclid força interessant per l'elevada toxicitat que presenta, també s'ha determinat l'activitat en diferents mostres biològiques (diferents peixos, cargol poma i musclos) que viuen aigües avall de la zona on hi ha ubicada la indústria de fosfat bicàlcic (Flix).

Continuant amb aquesta dinàmica i degut a que hem obtingut activitats elevades en els estudis anteriors de ^{210}Po en els musclos i el cargol poma, el segon bloc se centra en la caracterització radiològica de radionúclids naturals (^{210}Po, ^{210}Pb, ^{234}U, ^{238}U, ^{232}Th i ^{230}Th) en diferents espècies de mol·luscs (navalles, ostrons, musclos, cloïsses i cargols de mar) que es cultiven al delta de l'Ebre.

Cal remarcar que diversos estudis de la bibliografia han demostrat una relació entre la presència d'activitats industrials i l'obtenció d'elevades concentracions d'activitat de radionúclids naturals en mol·luscs [11,12]. Considerant que al llarg del riu Ebre hi ha diferents indústries, aquest estudi ens pot aportar una informació radiològica important pel que fa a la bioacumulació dels radionúclids naturals procedents principalment de la industrialització en aquests tipus d'organismes. Finalment, per tal de completar aquesta informació, s'ha fet una estimació de les dosis anuals envers als éssers humans que consumeixen aquests tipus d'aliments.

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3.1. Determinació de radionúclids procedents de la industrialització de l’últim tram del riu Ebre

Les plantes de tractament d'aigua potable (ETAP) generalment utilitzen l'aigua superficial del riu com a matèria primera. Encara que la concentració dels radionúclids a l'aigua superficial sol ser força baixa, mitjançant els processos de potabilització, els radionúclids s'eliminen de l'aigua i són concentrats als fangs. En estudis previs del nostre grup de recerca centrats en el desenvolupament de diferents mètodes analítics per a la determinació de la radioactivitat ambiental de la part final del riu Ebre, s'ha demostrat la presència d'alguns radionúclids naturals i d'artificials en els fangs de l'ETAP d'interès [1–4]. Per exemple, en l'estudi de Mola i col. [3] es va desenvolupar un mètode per a la determinació selectiva de ^{90}Sr mitjançat l'ús d'una reïna específica (Sr-spec) seguit d'un detector d'escintil·lació líquida. Les activitats obtingudes per aquest isòtop van ser entre 34 i 76 Bq/Kg, podent relacionar aquestes activitats amb la presència de la central nuclear aigües amunt del riu Ebre. Pel que fa als radionúclids naturals, un exemple és un estudi dels mateixos autors [4], on es comparen dos mètodes (un mètode clàssic amb l'ús d'una reïna, i un mètode automàtic amb un sistema multixeringa) per a la separació de forma selectiva dels isòtops d'urani i tori en les mateixes mostres de fangs de l'ETAP. Les activitats obtingudes per a l'^{238}U i ^{234}U van ser de 167 – 217 Bq/kg i 207 – 225 Bq/kg, respectivament. Mentre que, per als isòtops de ^{230}Th i ^{232}Th van ser de 4.0 – 9.7 Bq/kg i 26.0 – 37.3 Bq/kg, respectivament.

El primer estudi, esta basat en l'optimització d'un mètode per determinar dos emissors beta (^{55}Fe i ^{63}Ni), per tal d'obtenir més informació sobre la caracterització radiològica dels fangs generats a l'ETAP. En aquest estudi es van agafar mostres integrades dels fangs generats durant un mes, durant tres mesos diferents (agost, octubre i desembre de 2014).

A la bibliografia hi ha diferents estudis en què determinen ^{63}Ni i ^{55}Fe en mostres d'efluents de les centrals nuclears [5,6], així com també en mostres ambientals sòlides [7,8]. L'interès de la separació d'aquests dos radionúclids es deu a que tots dos són emissors beta i les seves energies d'emissió són molt properes. Per separar aquests radionúclids en mostres sòlides, hi ha diferents estratègies a la bibliografia que inclouen els passos següents: digestió de la mostra, separació de radionúclids i detecció. El procediment més comú per fer la separació del ^{55}Fe és mitjançant una reïna d'intercanvi aniònic, mentre que la separació de ^{63}Ni se sol fer mitjançant una precipitació del níquel amb una columna de DMG a pH 8-9. Finalment, la determinació es fa mitjançant un detector d'escintil·lació líquida [7,9,10]. Després de validar el mètode a través de mostres d'intercomparació, aquest va ser aplicat a la determinació de ^{55}Fe i ^{63}Ni en mostres de fangs procedents de l'ETAP. Els resultats obtinguts en aquest estudi s'inclouen en l'apartat 3.1.1 i han estat publicats a la revista *Journal of Radioanalitical and Nuclear Chemistry (online: 28 January 2016).*

Continuant amb l'objectiu de realitzar una caracterització radiològica exhaustiva dels fangs generats a l'ETAP, el següent treball d'aquest bloc se centra amb l'optimització d'un mètode per a la determinació selectiva d'un radionúclid natural en aquests fangs, el ^{210}Po. D'altra banda, en aquest treball s'ha aprofundit més amb la determinació d'aquest radionúclid en mostres de biota tals com musclos, peixos i cargols que viuen aigües avall de les indústries esmentades anteriorment (la indústria de fosfat bicàlcic i la planta de tractament d'aigua potable). L'interès d'aquestes mostres de biota recau amb la importància de verificar la possible influència de la indústria de fosfat bicàlcic en aquest tipus d'espècies. A més a més, algunes d'aquestes espècies (com els musclos) són consumides per la població en la seva dieta i per això és transcendent avaluar el seu contingut radiològic, ja que pot tenir un efecte sobre la salut de les persones que en consumeixen.

En aquest estudi, hem agafat dos tipus de mostres, líquides (aigua d'entrada i sortida de l'ETAP) i sòlides (fangs i biota) per avaluar el contingut de ^{210}Po. En el cas de les mostres de fangs de l'ETAP, s'ha agafat una mostra integrada mensual, durant 3 mesos diferents. En el cas de les mostres de biota, es van escollir tres espècies diferents de peix (silur, perca i carpa), una mostra de cargol poma (espècie invasora) i una mostra de musclo (de cadascuna de les badies del delta: Alfacs i Fangar).

Respecte a les fonts de ^{210}Po al medi ambient, cal destacar algunes activitats industrials així com també la geologia del terreny. Centrant-nos en les fonts industrials, un tipus són les indústries que no utilitzen materials pròpiament radioactius, però que a través dels seus processos concentren els radionúclids naturals en els residus o sub-productes [11]. Un exemple d'aquestes és la indústria de fosfat bicàlcic, i en aquest cas, cal destacar que al marge dret del riu Ebre, concretament a l'alçada de Flix, hi ha una planta on es produeix fosfat bicàlcic a partir de la reacció química de la roca fosfòrica amb àcid clorhídric diluït.

Pel que fa a la metodologia d'anàlisi de ^{210}Po, a la bibliografia hi ha diferents procediments per a la separació d'aquest isòtop. Per exemple, en el cas de mostres d'aigua, l'opció més habitual consisteix en la coprecipitació amb Fe^{3+} [12,13]. En canvi, en el cas de les mostres sòlides, s'ha d'afegir una digestió de la mostra [14,15]. Tant en les mostres líquides com sòlides, el ^{210}Po s'ha d'auto-depositar a planxetes de plata. En aquest cas, les condicions experimentals d'auto-deposició varien força en els diferents estudis [12,16–17], així doncs, en el nostre estudi s'han optimitzat les condicions per fer aquesta etapa (concentració de la solució, temperatura i temps). Un cop el ^{210}Po se separa de la matriu i és auto-depositat a les planxetes, la determinació es du a terme amb un detector d'espectrometria de partícules α. Els resultats obtinguts en aquest estudi s'inclouen en l'apartat 3.1.2 i han estat publicats a la revista *Journal of Environmental Science and Pollution Research 22 (24)(2015) 20032 – 20040.*

A continuació, tal i com s'ha comentat, s'inclouen els dos treballs que formen part d'aquest primer bloc d'estudis, amb l'interès de determinar els radionúclids procedents de la industrialització de l'últim tram del riu Ebre.

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3.1.1. Determination of artificial beta-emitters in sludge samples

DETERMINATION OF ARTIFICIAL BETA-EMITTERS IN SLUDGE SAMPLES

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Abstract

A method has been developed for the determination of two artificial beta emitters (^{55}Fe and ^{63}Ni) in sludge samples from a drinking water treatment plant (DWTP). The activities found for ^{55}Fe and ^{63}Ni ranged between (<15 Bq kg^{-1}) and 162 Bq kg^{-1}, and between (<10 Bq kg^{-1}) and 65 Bq kg^{-1}, respectively. Using the sludge activities is possible to estimate the activity of both radionuclides in the river water, based on the relation between the amount of sludge generated and the flow of the river water treated in the plant. Based on this estimation, it is possible avoid the use of time-consuming methods.

Keywords: *Iron-55, Nickel-63, sludge, drinking water treatment plant, nuclear power plant.*

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Introduction

Over the last few decades, increasing attention has been paid to the presence of natural and artificial radionuclides in different types of water samples [1–4]. On the whole, the origin of natural radionuclides in river water can generally be attributed to the geology of the land through which the rivers flow. However, another factor that can contribute is the presence of different industries, known as Naturally Occurring Radioactive Materials (NORM) industries that, during their processes, concentrate certain natural radionuclides in the waste that they produce. Meanwhile, artificial radionuclides can originate from three different main sources: nuclear weapons testing, accidental release from nuclear power plants (NPP) and radioactive effluents from nuclear facilities. However, in general, the activities of these radionuclides in environmental water samples are low (at levels of mBq L^{-1}) in comparison to those of natural radionuclides.

In the literature, there are various different studies about the determination of artificial radionuclides such as tritium, strontium and caesium, among others, in environmental solid and water samples collected in zones influenced by NPPs [5–11]. For example, tritium has been quantified in different rivers across Europe, such as the Ebro in Spain [9], the Danube in Serbia [10] and the Yenisei in Russia [11]. In the study conducted in Serbia, the activity found was around 3 Bq L^{-1}. However, in the case of the Russian study, the activities rose to as high as 170 Bq L^{-1}. In all these cases, there is at least one NPP along the course of the river. As far as solid samples are concerned, in sediment samples from different rivers, the presence of artificial radionuclides such as ^{137}Cs, ^{54}Mn, ^{152}Eu, ^{65}Zn, ^{60}Co, among others, has been confirmed in different studies at activity concentration levels of low Bq kg^{-1} [6, 7].

Drinking water treatment plants (DWTP) generally use surface water as raw water. Although the concentration activity for the different isotopes that can be normally found in these waters is usually low, these radionuclides can effectively be removed from the water through the different treatments applied in these plants. However, one consequence of this is that these isotopes are concentrated in the sludge generated during the process, as can be seen in previous studies by our group [9, 12, 13], in which the presence of different natural and artificial radionuclides has been demonstrated. In the case of the latter, ^{137}Cs, ^{90}Sr and ^{60}Co were identified and quantified and their origin may be related to the presence of a NPP upstream of the river. For example, in the study by Mola *et al.*

[13], an automatic extraction method using a specific resin (Sr-spec) followed by liquid scintillation counting (LSC) detection was used to determine the presence of ^{90}Sr in the sludge generated in a DWTP in Spain that uses water from the River Ebro as raw water and, moreover, this plant is located downstream of a NPP. The activity concentrations found for this isotope in the analysed samples ranged between 34 and 76 Bq kg^{-1}.

In the present study, in order to obtain more information about the radiological characterization of the sludge generated at the same DWTP, our research has focused on the development of a method to determine two artificial beta emitters (^{55}Fe and ^{63}Ni) in these solid samples. Iron and nickel are constituents of a wide range of construction materials in the nuclear industry and their corresponding activation products are often encountered in solid radioactive waste and effluents. In some cases, these products can be discharged into the environment by NPPs [14, 15]. ^{55}Fe is an activation product and a low-energy beta emitter with a half-life of approximately 2.7 years. It is present in radioactive wastes and must be attributed to the fact that iron is a major constituent of the structural materials used in pressurized water nuclear power plants [16]. Meanwhile, ^{63}Ni is a pure beta emitter with a half-life of approximately 98.7 years and it is mainly produced in nuclear reactors as an activation product as a result of ^{62}Ni and ^{63}Cu reactions.

In the literature, there are various different studies in which ^{63}Ni and ^{55}Fe have been determined in water samples collected from different effluents from NPPs [17, 18]. In addition, these isotopes have also been determined in different environmental solid samples, such as moss, soil, marine fauna, fish and sediments [19–21]. With respect to these solid samples, there are different strategies reported in the literature, all of which involve the following steps: digestion of the sample, isolation of the radionuclides and, finally, their detection. For the digestion of the sample, acidic digestion is the preferred choice, usually involving a mixture between HCl and HNO_3 of different compositions. Subsequently, for the isolation of ^{63}Ni and ^{55}Fe, there are different strategies. In the case of ^{55}Fe, the usual process is to use a Biorad resin, an anionic exchange resin (Biorad AG1-X8), while for ^{63}Ni, a resin containing dimethylglyoxime (DMG) coated on an inert support is normally used. This process is based on the on-column precipitation of nickel with DMG at pH 8-9. Finally, in the detection step, liquid scintillation counting is the preferred choice for both radionuclides [15, 19, 20, 22, 23].

Based on all of this, the main aim of the proposed study is to make further advances in the radiological characterization of the sludge samples generated at DWTPs, while also estimating the presence of these compounds in river water.

Experimental part

Reagents and standards

All chemical reagents and solutions used in this study were of analytical grade. HCl (35%), HNO_3 (65%) and NH_4OH (28%) were supplied by J.T. Baker (Deventer, Holland). The liquid scintillation cocktails used were Optiphase Hifase 3 and Ultima Gold LLT, supplied by Perkin Elmer (Waltham, USA). Polyethylene (PE) scintillation vials were supplied by Sarstedt (Nümbrecht, Germany). Ammonium citrate dibasic ($HOC(CO_2H)(CH_2CO_2NH_4)_2$), $NiCl_2$ and $FeCl_3$ were supplied by Sigma-Aldrich (Steinheim, Germany). Biorad AG1-X8 resin (100-200 μm mesh chloride form) and Ni-resin (100-150 μm) were supplied by Eichrom (France), and glass fibre pre-filters were purchased from Millipore (Madrid, Spain).

Standard solutions of ^{55}Fe and ^{63}Ni used for the calibrations were provided by Eckert and Ziegler (Braunschweig, Germany). The certified nominal activity for ^{55}Fe was 41 ± 1 kBq g^{-1}, while for ^{63}Ni, it was 41 ± 1 kBq g^{-1}.

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Uranium was electroplated onto stainless steel planchets (diameter 25.15 mm and thickness 0.6 mm) supplied by Tecnasa (Madrid, Spain). Samples were filtered with a 0.45 μm filter supplied by Whatman (Maidstone, United Kingdom).

For the measurement of ^{222}Rn, Teflon-coated polyethylene vials with a volume of 20 mL were used, equipped with urea screw caps and aluminium foil liners. They were supplied by Perkin Elmer^{TM}.

Instrumentation

The Speedwave microwave digestion system equipped with 12 pressure vessels of Teflon was supplied by Berghof (Eningen, Germany). This system was used for the digestion of the sludge samples from a DWTP.

An ultra-low-background Quantulus 1220^{TM} liquid scintillation spectrometer (Perkin Elmer) was used for measuring ^{55}Fe and ^{63}Ni. It was equipped with three sample tray tables of 20 positions and the EASY view spectrum analysis programme.

An atomic absorption spectrometer (AAS), the Unicam 969 AA spectrometer Solar (Thermo Scientific, Waltham, MA, USA), was used to calculate the chemical recovery of the stable iron and nickel in the extraction process. The optimal wavelength used was 248.3 nm for iron and 232.0 nm for nickel.

A P-Selecta centrifuge equipped with four 50 mL glass tubes was supplied by JP SELECTA S.A (Barcelona, Spain).

Samples

In this study, the presence of ^{55}Fe and ^{63}Ni was evaluated in sludge samples obtained from the water treatment process in a drinking water treatment plant (DWTP) located in L'Ampolla (Tarragona, Spain). These samples were a mix of a composite sample of the sludge generated over the course of one month, and samples were collected in three different months (August, October and December 2014). 500 g of sludge sample was dried at a temperature of 110ºC in a stove. Afterwards, the samples were crushed in a ball mill and sifted in a sieve of 250 µm, and then finally stored in a plastic container.

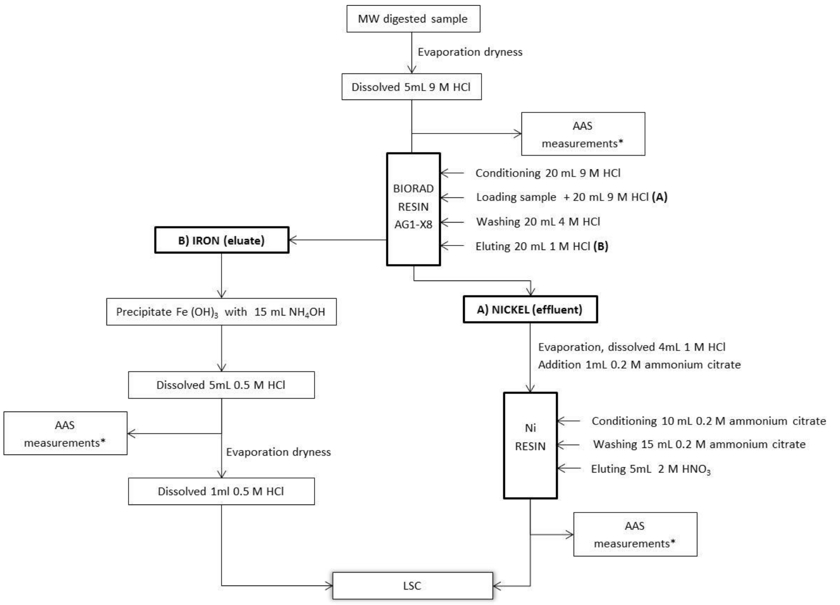
Analytical procedure

A basic diagram of the procedure is shown in Figure 1. The sample preparation consists of different steps. After the sludge sample was calcinated in the muffle furnace for 12 hours at 700ºC, 150 milligrams of sample were introduced into a vessel and 1 mL of the standard of 1000 mg L^{-1} of $NiCl_2$ was added in order to calculate the nickel recovery. The digestion was performed with 15 mL of a mixture of nitric acid and hydrochloric acid (3:1) using the microwave system which has reported recoveries higher than 90% [24, 25]. The vessel was then placed in the microwave oven set at a power of 900 W with an initial temperature of 50ºC. The temperature ramp was 10ºC min^{-1} up to 175ºC, at which point it was held for 30 minutes before the cooling process. The total digestion time was 60 minutes. The sample was then filtered using a 45 µm filter and then evaporated until dryness using a sand bath. Finally, the residue was dissolved in 5 mL of 9 M HCl.

The extraction/separation process is as follows. Firstly, 10 g of Biorad AG1-X8 resin was mixed with 100 mL of water and stirred for 30 min and then it was introduced in a glass column (20 cm length and 10 mm internal diameter) and conditioned by passing through 20 mL of 9 M HCl. The second step was to load 5 mL of sample (dissolved in 9 M HCl) and, at this point, it should be noted that the elution of the sample loading (aliquot A) must be collected because nickel is not retained in that column. Once the sample is loaded, the clean-up step consists of the use of two different acids. Firstly, 20 mL of 9 M HCl was used, and this fraction was also collected and mixed with the previous aliquot (aliquot A) to ensure that all of the nickel was recovered. The second acid used in the clean-up was 20 mL of 4 M HCl to remove the possible interferences retained in the column, and this fraction was discharged. Lastly, the elution of Fe from the Biorad AG1-X8 resin was carried out using 20 mL of 1 M HCl.

In the fraction eluted with Fe, 15 mL of concentrated NH_4OH was added and the mixture was then heated for 15 min in order to precipitate the iron as iron hydroxide. After that, the sample was centrifuged for 10 min at 5.000 rpm. The supernatant was discharged and the precipitate was redissolved in 5 mL of 0.5 M HCl. At this point, in order to calculate the recovery of iron, 0.1 mL of that sample was diluted in distilled water and then the concentration of iron was measured by AAS. The rest of sample was evaporated until dryness and redissolved with 1 mL of 0.5 M HCl and mixed with 19 mL of the scintillation cocktail (Optiphase Hifase 3) for the LSC measurement of ^{55}Fe.

Aliquot A and the clean-up fraction of the Biorad AG1-X8 resin (containing the nickel) were evaporated until dryness and redissolved in 4 mL of 1M HCl and 1 mL of 0.2 M ammonium citrate, and then the pH was adjusted to a value of 8-9 using NH_4OH. The conditioning of the 300 mg Ni-resin was performed with 10 mL of 0.2 M ammonium citrate (pH 8-9). After that, 5 mL of sample was loaded and then the clean-up was performed, consisting of passing through 15 mL of 0.2 M ammonium citrate (pH 8-9). The last step was



* AAS measurements to calculate recovery of the extraction process.

Fig 1. Basic diagram of the analytical procedure followed in the determination of ^{55}Fe and ^{63}Ni in sludge samples from a DWTP.

conducted using 5 mL of 2 M HNO_3 as the elution solvent and, finally, 1mL of the eluted fraction was used to calculate the recovery in the extraction process by means of AAS analysis.

The rest of the sample (4 mL) was mixed with 16 mL of the scintillation cocktail (Optiphase Hisafe 3) for the LSC measurement. All of the samples were measured one week after the separation in order to avoid chemiluminescence overlapping the ^{55}Fe spectrum.

Recovery measurement

In order to calculate the recoveries of the iron and nickel extraction process we used two different strategies. First of all, for nickel extraction, the samples were spiked before the calcination step by using 1 mL of a standard of 1000 mg L^{-1}. After the extraction process in the elution of the Ni-resin, 1 mL of the extract was used to calculate the recovery by means of an AAS analysis.

In the iron case, due to the high content of iron in the sludge samples due to the coagulation and flocculation steps carried out in the water treatment, we cannot use the same method as nickel. So, in this case, in order to calculate the iron recovery, we measured the concentration of iron before and after the extraction process. In this sense, we took 0.1 mL of the sample (with 9 M HCl) and was mixed with Milli-Q water to reach a volume of 25 mL and iron was measured by AAS. Moreover, iron was also measured from the sample obtained after the extraction process as it is shown in Figure 1.

Results and Discussion

LSC optimization

As mentioned in the Introduction, in terms of the different detectors used to determine beta emitters, the preferred choice in the literature for the determination of ^{63}Ni and ^{55}Fe is liquid scintillation counting [15, 17, 19, 20, 23]. However, in these studies, low efficiency has been achieved for ^{55}Fe detection (20%), mainly due to the low range of energy of ^{55}Fe. In order to determine whether this can be improved, different conditions were evaluated that may have an effect of efficiency. In this case, different combinations of volumes of 0.5 M HCl were used, which is the medium used for ion elution from the resin, as well as two scintillator cocktails (Optiphase Hisafe 3 and Ultima Gold LLT), which has been previously used in literature, with satisfactory results being obtained [15, 17, 19]. The highest efficiency for ^{55}Fe was achieved when 1 mL of sample and 19 mL of Optiphase Hisafe III were used and the efficiency obtained in this case was 22 ± 2%. The background counts obtained for ^{55}Fe in this optimized method were 0.518 cpm.

The efficiency reported for ^{63}Ni in different studies in the literature was higher than for ^{55}Fe, with values up to 60% [15, 23]. In the case of ^{63}Ni, the most usual scintillation cocktail used is Optiphase Hisafe 3 and, as such, in the present study, it was mixed with different volumes of 2 M HNO_3. The best efficiency was obtained using the combination of 4 mL of sample and 16 mL of Optiphase Hisafe 3, at 55 ± 5%, which is similar to the values reported in the literature. The background counts obtained for ^{63}Ni in this optimized method were 0.766 cpm.

Iron Extraction

To extract the iron from sludge samples, a Biorad AG1-X8 resin was used. According to the literature [26–28], when using this resin, it is possible to separate between ^{55}Fe and ^{63}Ni radionuclides, as it has been demonstrated that, if the initial sample is dissolved in 9 M HCl, iron can be retained in the anionic exchange resin but this does not happen in the case of nickel.

The optimization of the process with the Biorad AG1-X8 resin was performed with standards in order to obtain a high recovery value for stable iron. In this case, the acid concentration was fixed at each step of the extraction process according to the conditions used in the study by Hou *et al*. [15], in which ^{55}Fe and ^{63}Ni were extracted. In our case, the effect of the volume of acid used was evaluated. The conditioning of the resin was performed using 20 mL of 9 M HCl. The volume of the sample was studied at 5, 10 and 20 mL of 9 M HCl in order to obtain the maximum retention of iron in the resin. To evaluate the optimal volume, the fraction of the sample was analysed after passing it through the column, while the iron concentration was analysed using atomic spectrometry. In this case, for all of the tested volumes, it was observed that iron was completely retained, as the measured concentration in the elution fraction was negligible. Based on these results, a volume of 5 mL was selected as it is enough to solubilize the residue and enables a lower amount of acid to be used in this step.

After the loading of the sample, a double step procedure was applied. The first step consisted of eluting the rest of nickel that can be present in the column. This was performed by passing 20 mL of 9 M HCl through the column. The second step was the clean-up using 20 mL of 4 M HCl. In both cases, the fractions were analysed and the stable iron was not eluted from the resin under all of the tested conditions and good recovery for nickel was achieved.

The elution of the retained iron was performed using 20 mL of 1 M HCl. Although a lower volume of acid (10 mL) was tested in order to reduce the residues and the associated risk, poor recoveries (lower than 40%) were obtained, whereas, at a volume of 20 mL, the recoveries were higher than 80 ± 3% (n=3).

Nickel extraction

In the case of the ^{63}Ni determination, only one specific resin (Ni-resin) has been reported previously in the literature [15] and, for this reason, its was selected for this study. In the optimization process, the same solvents we selected as previously reported but the effect of different solvent volumes on the recovery process was evaluated. The sample eluted in previous study using Biorad AG1-X8 resin was adjusted to pH 8-9 with 0.2 M ammonium citrate previously treatment with specific resin (Ni-resin).

Ni-resin was conditioned using 10mL of 0.2 M ammonium citrate (pH 8-9) and then the sample (diluted in 5mL) was added. The clean-up step consists of 5 mL of 0.2M ammonium citrate (pH 8-9) and the elution was performed using 5 mL of 2 M HNO_3. Under these initial conditions, the recovery of nickel in the elution step was 78 ± 5% (n=4). Although a number of attempts were carried out to increase the recovery by changing the volumes of the different solvents, no improvements were observed, so these conditions were maintained. Under the optimal conditions found for the extraction of both isotopes from water spiked samples, the same procedure was then evaluated for solid samples obtained from an intercomparison exercise.

Method validation

In order to test whether the method can be applied to solid samples, the method was validated using a solid sample from an intercomparison exercise organized by the Nuclear Safety Council of Spain (CSN) in 2012, which was a soil with a content of 70% of carbonates that contained low levels of anthropogenic and natural radionuclides. The sample was composed of a mixture of different contaminated and uncontaminated soils. The soil contained 249 ± 13 Bq kg^{-1} and 52 ± 3 Bq kg^{-1} of ^{55}Fe and ^{63}Ni, respectively.

The mean results for three replicates (n=3) were 206.9 Bq kg^{-1} and 52.3 Bq kg^{-1} for ^{55}Fe and ^{63}Ni, respectively (the measurement was carried out one week after separation). The Z-scores obtained were -1.7 and 0.1, respectively. The uncertainties (K=2) ranged between 13 and 22 Bq kg^{-1} (6-11%) for ^{55}Fe and between 5.3 and 5.8 Bq kg^{-1} (10-11%) for ^{63}Ni. Table 1 shows the corresponding values obtained for the determination of ^{55}Fe and ^{63}Ni in the intercomparison sample when three different individual measu-rements were performed.

After the validation of the extraction and LSC measurement, the method developed was used to determine ^{55}Fe and ^{63}Ni in different sludge samples generated at the DWTP in L'Ampolla.

Study of the interferences due to chemiluminiscence in sludge samples

The next step focused on the determination of both isotopes in sludge samples from a DWTP. In particular, samples were analysed from the DWTP in L'Ampolla, which treats water from the River Ebro in a plant downstream from a NPP (Ascó). Unfortunately, in these sludge samples, the quantification of ^{55}Fe was not possible as a broad peak appeared in the corresponding spectra in the range of energies at which this isotope is determined. Fortunately, when the measurements were carried out one week after the separation, this problem was avoided, so, after this time, the measurement of ^{55}Fe was possible.

In order to reduce the time between sample preparation and measurement, the possible causes of this interfering peak found in the spectra were evaluated. There are two main interferences in LSC measurements: photoluminescence and chemiluminescence. In order to ascertain which kind of interference was the cause of our problem, firstly, the samples were kept in the dark overnight prior to LSC measurement in order to verify whether the interference was due to photoluminescence effects. However, when the sample was kept in the dark and measured on two consecutive days, the interference did not disappear completely. Therefore, further studies had to be performed to investigate the possibility of a chemiluminescence problem, as has already been reported by Geckeis *et al.* [29]. In the case of

Table 1. Results obtained for ^{55}Fe and ^{63}Ni activity concentration (Bq Kg^{-1}) in the analysis of the intercomparison sample organized by the CSN in 2012.

		Reference activity	Calculated activity	Recovery (%)	Uncertainties	Trueness (%)	Z-score
^{55}Fe	Sample 1	249	204	69	22	18	1.8
	Sample 2		210	68	13	16	1.6
	Sample 3		208	68	15	16	1.7
	Average		*206.9*	-	-	*17*	*1.7*
^{63}Ni	Sample 1	52,4	54.1	83	5.3	3.2	0.3
	Sample 2		50.6	97	5.8	3.4	0.3
	Sample 3		52.1	89	5.7	0.6	0.1
	Average		*52.3*	-	-	*0.2*	*0.1*

chemiluminescence, it should be pointed out that, in this case, the amount of interference is directly related to the amount and type of sample used and the properties of the interfering component. An increase in the kinetics of the chemiluminescence reaction in the sample may help to solve this problem. Geckeis *et al.* also highlight that this considerable interference observed in ^{55}Fe measurements appears particularly at high Fe (III) concentrations, as is the case of our sludge samples which ranged between 100 and 120 mg L^{-1} of stable iron, since $FeCl_3$ is used as coagulant in the process carried out at the plant.

In order to ascertain whether the interference was produced by a chemiluminescence effect, as the literature seemed to suggest, particularly in view of the composition of the analysed samples, a soil sample was analysed from an intercomparison exercise organized by the Nuclear Safety Council of Spain (CSN) in 2012 with 249 ± 13 Bq kg^{-1} and 53 ± 3 Bq kg^{-1} of ^{55}Fe and ^{63}Ni, respectively. The first measurement was performed 3 hours after the preparation. The samples were then kept at different temperatures (6ºC, 20ºC, 40ºC, 60ºC and 80ºC) for approximately 8 hours and were then introduced into the instrument 3 hours before counting in order to achieve ambient temperature. This procedure was repeated daily so that the measurement of each sample could be performed on four consecutive days. Between measurements, the samples were kept at a specific temperature. Figure 2 shows the count rate obtained in the different measurements for iron determination at the different temperatures. A difference could be observed in the slope of the curves obtained and the effect of the temperature in the reaction. Based on the graph, it is possible to observe that, when the sludge samples were kept at high temperatures such as 40ºC and 60ºC, the samples could be measured faster, as the interfering peak disappeared sooner in comparison to the measurement with the samples kept at ambient temperature. However, the stability of the scintillation cocktail is not guaranteed, as the sample/liquid scintillation mixture displayed a soft

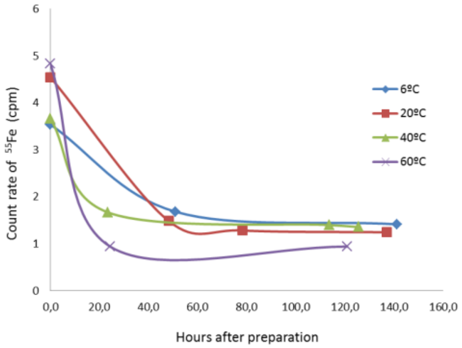


Fig.2. Count rate in the LSC measurement of iron when the intercomparison sample was kept at different temperatures (6ºC, 20ºC, 40ºC and 60ºC).

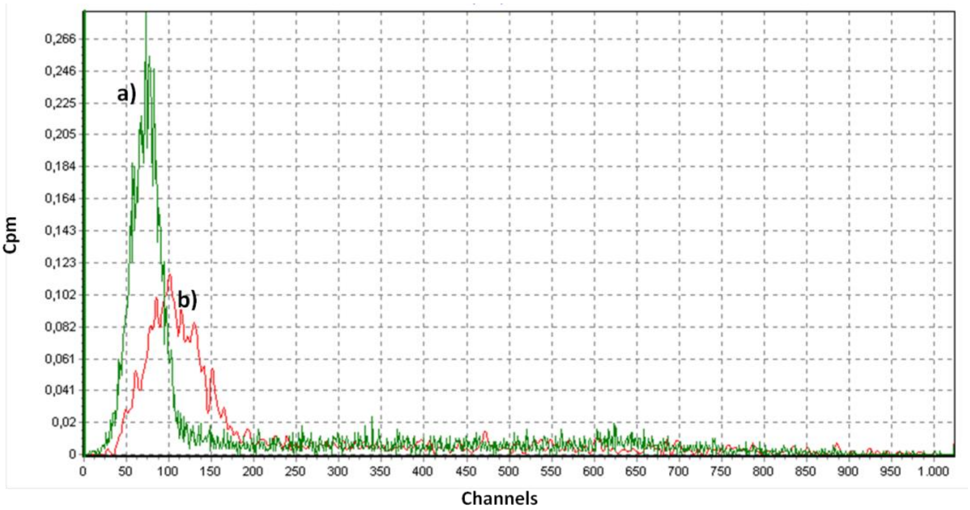


Fig.3. LSC spectra of ^{55}Fe from a sludge sample from the DWTP (a) after preparation of the sample, (b) a week after preparation.

yellow colouration after 150 hours at 60ºC. At the higher temperature (80ºC) the scintillation cocktail is degraded, so the quantification was also not possible. Taking these results into account, the vials were stored for one week prior to measurement at ambient temperature, as no degradation problems were observed at this temperature. Figure 3 shows a LSC-spectrum from a sludge sample measured after the preparation (which displayed high chemiluminescence) and a week after the preparation (without chemiluminescence).

In addition, in order to verify if the presence of iron in the sludge samples was the main reason for the present of chemiluminescence, a set of measurements were carried out with a simulated water matrix containing increasing amounts of iron salt (between 1 to 5 mg of stable iron) in the same ratio as the samples (1:19 mL). Figure 4 shows the results obtained and it can be observed that higher concentrations of iron also increased the count rate of the interfering peak in the LSC spectra. As the element responsible for the chemiluminescence is iron, it was concluded that the interference can only be avoided by measuring the samples one week after preparation, when the chemiluminescence reaction has finished.

Analysis of sludge from a DWTP

In previous studies by our research group focusing on the determination of different isotopes in sludge samples

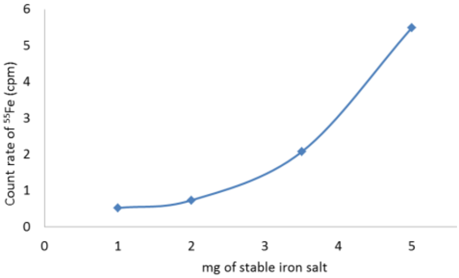


Fig.4. Influence of the amount of iron on the LSC measurement.

from the DWTP located in L'Ampolla (Tarragona, Spain), the presence of different artificial radionuclides could be observed, such as ^{60}Co, ^{110m}Ag, ^{137}Cs and ^{57}Mn, at low activity concentrations levels [9, 30]. The presence of such radionuclides may be related to the presence of a Nuclear Power Plant (NPP) in Ascó with two pressurized water reactor units. This NPP is located upstream of the DWTP and, in the course of its routine operation, it discharges different isotopes in waste streams that reach the River Ebro. Consequently, these isotopes can be transported to the DWTP where they are concentrated in the sludge generated. Our aim is to determine ^{55}Fe and ^{63}Ni in this sludge in order to gather more information about its radiological content, as well as estimating the presence of these compounds in river water.

To this end, three different sludge samples from the DWTP were analysed. Three different months were selected between August and December 2014. The results obtained are summarized in Table 2. Firstly, as can be observed in the table, the maximum activity concentration found for both ^{55}Fe and ^{63}Ni were in October, at concentration levels of 162 and 65 Bq kg^{-1}, respectively. Secondly, ^{55}Fe and ^{63}Ni showed an activity lower than the minimum detectable activity (MDA) in the sample from August which was 15 and 10 Bq kg^{-1} for ^{55}Fe and ^{63}Ni, respectively.

Furthermore, based on the data that

Table 2. ^{55}Fe and ^{63}Ni average activity concentration values (n=3) in Bq/Kg obtained for sludge samples from the DWTP in L'Ampolla during the analysed period and estimated values of activity obtained for water samples from the River Ebro in mBq/L.

	August 2014		**October 2014**		**December 2014**	
	Sludge	**River***	**Sludge**	**River***	**Sludge**	**River***
^{55}Fe	< 15	<0.2	162 ± 20	2.2	62 ± 15	0.9
^{63}Ni	< 10	<0.1	65 ± 9	0.9	26 ± 8	0.4

* estimated value

every 1 m^3 of raw water that enters the DWTP generates 14 g of sludge, it may be estimated that the maximum activity found in the sludge in October can be related to an activity in the river water of around 2.5 and 1 mBq L^{-1} for ^{55}Fe and ^{63}Ni, respectively. This theoretical estimation of the activity levels for both isotopes in river water can be considered an extremely useful tool, as it enable the analysis of these water samples to be avoided, thereby saving time and money. Moreover, to be able to quantify these isotopes at the low levels at which they are present in these samples, a high sample volume or long counting time would be necessary. In this respect, Skwarzec *et al.* [21] determined the presence of both radionuclides in environmental samples, such as seawater, and, in order to obtain a minimum detectable activity between 1 and 2 mBq L^{-1}, a counting time of 3000 minutes was needed, with 10 L of natural water as the sample volume, making this procedure time-consuming.

Conclusions

In this study, a method has been developed to determine ^{55}Fe and ^{63}Ni in sludge samples generated at a drinking water treatment plant. The method was validated using a soil sample from an intercomparison exercise containing both radionuclides. To the best of our knowledge, this study has demonstrated for the first time the presence of these radionuclides in this kind of sample at concentration levels up to 162 and 65 Bq kg^{-1}, for ^{55}Fe and ^{63}Ni, respectively. After observing different problems in the quantification of the sample, the presence of chemi-luminescence interference was confirmed in the case of ^{55}Fe determination, due to the high content of iron (III) in the sludge. Keeping samples at 40ºC to 60ºC for 8 hours helps to accelerate the decay of the interference. However, the stability of the scintillation cocktail is not guaranteed, so measurements of the samples were taken one week after separation, as this was the best approach to overcoming the chemi-luminescence issue in this study.

Using the activity concentration found in the sludge samples analysed, the initial concentration in the river water used by the DWTP could be estimated. It also enabled the activity of the NPP activity to be controlled, thereby avoiding time-consuming methods to determine these radionuclides in water samples.

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3.1.2. Polonium-210 levels in different environmental samples

POLONIUM-210 LEVELS IN DIFFERENT ENVIRONMENTAL SAMPLES

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Abstract

Polonium-210 is analysed in different samples which can be affected by the presence of a dicalcium phosphate plant (DCP). Particularly was determined in sludge from a drinking water treatment plant located downstream of the phosphate plant. The activity values found were comparable to activities expected in normal soil. This isotope was also monitored in different biota species (as mussels) taken also downstream of the DCP and evaluate the potential risk of their ingestion by calculating the total effective doses. As a result we could observe that the ingestion of these mussels does not constitute a risk since the found doses were lower that the values published by UNSCEAR.

Keywords: *^{210}Po, alpha spectrometry, microwave digestion, naturally occurring radioactive material, biological samples, drinking water treatment plant.*

Highlights

- Polonium was determined in different samples from the drinking water treatment plant (DWTP) as sludge, influent and effluent water.
- Also polonium was determined in order to monitoring this isotope in biota samples taken downstream of the dicalcium phosphate plant (DCP).
- The annual effective dose was calculated in order to evaluate a potential risk due to biota species ingestion.
- The ingestion of these mussels does not constitute a risk since the found doses were lower that the values published by UNSCEAR.

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Introduction

^{210}Po is a isotope from ^{238}U decay chain and has a half-life of 138 days. It is considered to be one of the most toxic naturally occurring radionuclides, and one of the most important environmental radionuclides due to its wide distribution and potential for human radiation exposure through ingestion and inhalation (Lin and Wu 2009; Aközcan 2013). In the marine environment, ^{210}Po is strongly accumulated in marine biota and transferred to man through ingested food so it is considered to be the most important radiation dose contributor received by humans via fish and shellfish consumption (Carvalho 2011; Rozmaric et al. 2012; Aközcan 2013; Kilic et al. 2014; Kristan et al. 2015).

The methods described in the literature for the determination of this isotope involve different steps. One of the required steps is a separation of ^{210}Po from the matrix before its quantification by alpha spectrometry. As it has been reported in the literature, this separation can involve several steps depending mainly on the matrix. For example, in the case of water samples, the preferred choice is usually a co-precipitation with Fe^{3+} (Benedik et al. 2009; Lee et al. 2010). For solid samples, an additional digestion step has to be included, and for that the preferred choice is a microwave digestion using a closed vessel (Sánchez-Cabeza et al. 1997; Matthews et al. 2007; Henricsson et al. 2011; Planisek et al. 2013). Once isolated from matrix, determination of ^{210}Po is usually carried out by α-particle spectrometry using a silicon surface barrier or passivated implanted planar silicon (PIPS) detectors (Desideri et al. 2007; Jia et al. 2009; Lin and Wu 2009; Henricsson et al. 2011; Baumann et al. 2013).

Regarding to the possible sources of ^{210}Po in the environment, it is important to highlight certain industrial activities. In this respect, it is worth mentioning activities that involve the use of different materials, usually regarded as non-radioactive but which contain naturally occurring radionuclides. Due to the processes involved, these industries can lead to a significant increase of the levels of these isotopes and, as a consequence, there is a potential increase in the exposure of workers or members of the public. One example of this type of industries is dicalcium phosphate production plants (DCP). In fact, we can highlight the presence of a DCP in the North Eastern part of Spain, in particular in Flix which for a long time discharged solid and liquid wastes into the Ebro River with no or minimal controls and, as a consequence, a highly contaminated area resulted from its activity. For this reason, a decontamination process of the affected area is currently being carried out. The main objective of this decontamination project is the removal of the contaminated sludge, which will subsequently be treated and stored in a dumping area. Moreover, the water generated in the treatment of the sludge is going to be treated and returned to the river and, consequently, the Ebro River and its ecosystem will be restored (Palomo et al. 2010a; Mola et al. 2011).

Downstream of this DCP there is a drinking water treatment plant (DWTP of L'Ampolla) which takes water from Ebro River as incoming water. Due to the treatment performed in this plant, most of the contaminants which can be present in the raw water can be eliminated but on the other hand they can be concentrated in the generated sludge. In previous studies of our research group, it has been demonstrated that, in sludge samples taken from this DWTP, different natural isotopes could be quantified, such as ^{234}U, ^{238}U, ^{230}Th, ^{228}Ac, ^{214}Pb and ^{214}Bi, among others (Palomo et al. 2010b; Palomo et al. 2010c) and their origin was attributed to the quality of the raw water treated in the plant, which is dependent on the geology of the area where this water flows, as well as on the industrial activities and decontaminated areas present along the course of the river such as the DCP. In these previous studies ^{210}Po was not included in the group of evaluated radioisotopes despite of the study of Casacuberta et al. (2010) which demonstrated its presence in products and wastes of the DCP industry.

Based on all of this, our main purpose is to determine this isotope in the sludge samples generated in the DWTP to have a more complete radiological information which can be very useful in case of a possible reusal. In this sense, the sludge generated in this plant of L'Ampolla was previously used as raw material in the production of cement and at the present moment is used in the environmental restoration of quarries, so it is extremely important to assure its radiological quality . On the other hand, another proposed aim has been focused in the determination of the activity concentration of this isotope in some biota samples as mussels and fish taken also downstream of the location of the DCP. The interest of these biota samples is from one hand to verify the possible influence of the DCP plant in different kind of species and on the other hand some of these species as mussels are consumed by the population so their radiological content can affect the people health.

Material and methods

Instrumentation

Polonium was measured using an alpha-spectrometer (EG&ORTEC, Model 676A), which include an ion-implanted silicon detector (ORTEC, size: 450 mm^2;

alpha resolution: 25 keV FWHM at 5.48MeV of ^{241}Am) in a vacuum chamber (Edwards, Model E2M8), a detector bias supplier, a preamplifier, a linear amplifier, and a multichannel pulse height analyser.

The calibration was done using a stainless steel planchet with certified activities for ^{233}U, $^{239/240}$Pu and ^{241}Am obtaining efficiencies oscillated between 14.79% and 17.33%. During the measurement, the pressure of the chamber was kept at 10^{-2} Torr. The counting time was 200,000 s.

To measure the turbidity a Turbidimeter Model 2100N supplied by Hach (USA) was used. This instrument is equipped with a stable halogen-filled tungsten filament lamp.

Microwave digestion of samples was conducted using a commercial MWS4 Speedwave oven supplied by Berghof (Eningen, Germany). For each run, twelve Teflon vessels were placed on a rotating turntable for homogenous heating.

Materials and reagents and equipment

All chemical reagents used in this study were of analytical grade. Hydrochloric acid (37%), nitric acid (65%), hydrogen peroxide (30%), ammonia solution (25%), acetone and iron chloride (III) were supplied by J.T. Baker (Holland). Ascorbic acid (99.7%) was supplied by Merk (Darmstadt, Germany).

^{210}Po was auto-plated onto silver discs (diameter 25.15mm and thickness 0.6mm) supplied by Goodfellow (Huntingdon, England). Samples were filtered with a 0.45µm cellulose filter supplied by Whatman (Maidstone, England).

To evaluate the alpha procedure recovery, ^{209}Po certified solution with activity concentration value of 23.46 ± 0.80 Bq/l was used.

Samples

Two types of samples, liquid (water) and solid (sludge and biological), were evaluated for their ^{210}Po content in this study. In the case of water samples, influent (Ebro river water) and effluent water were analysed from the DWTP located in L'Ampolla (Tarragona, Spain). Influent water was collected directly of Ebro river in Campredó, 75 km downstream from the DCP, while effluent water (potable water) was collected at the DWTP. 4 L of water were collected weekly from the main pipe of influent and effluent water, between November 2014 and February 2015.

Sludge samples were collected from the DWTP in four different months (November 2014 to February 2015). 500 g of the sludge was taken every day from the centrifuge for a month and at the end of this period the sludge was transported to the laboratory. Then, the sludge was transferred to a tray and dried in an oven at a temperature of 80ºC. The samples were then crushed in a ball mill and sifted in a 250 µm sieve.

In the case of biological samples, different species were collected. These included three different fish species (catfish, perch and carp), they were collected in the Ebro River in an area between the DCP and the DWTP. Moreover, a recent introduced invasive species (apple snail) was also analysed. To collect apple snails due to is invasive species we need a special permission by *Departament d'Agricultura, Ramaderia, Pesca, Alimentació i Medi Natural (Generalitat of Catalunya).* In addition, mussel samples were collected by the *Institut de Recerca i Tecnologia Agroalimentàries (IRTA)* in June 2014 from the Fangar and Alfacs bays of the Ebro River Delta. In Figure 1 all the areas from where samples were taken are shown. On the other hand a control group of mussels (from Galicia) was bought in a fish market. Then, biological samples were dried in an oven at a temperature of 80ºC and crushed in a ball mill and sifted in a 250 µm sieve.

Analytical method for liquid samples

Four liters of water sample was taken in a beaker, and then, 0.5 mL of ^{209}Po (23.46 ± 0.80 Bq/L) was added as internal tracer, as well as 10 mL of HCl 37% (pH 1-2) to prevent losses through surface adsorption and to guarantee the equilibrium between ^{210}Po and ^{209}Po.

The method used is a co-precipitation of polonium in hydroxide form with $FeCl_3 \cdot 6H_2O$ (Benedik et al., 2009; Díaz-Francés et al., 2013; Lee et al., 2010). To achieve this, 3mL from a solution of $FeCl_3 \cdot 6H_2O$ (30000 ppm) was added together with NH_4OH until a pH value of 8 was reached, and then the hydroxides were precipitated. The solution was then kept in the fridge overnight, allowing the hydroxides to settle. Subsequently, the supernatant was siphoned off and the precipitate was centrifuged. Finally, the supernatant was removed by decantation and the precipitated hydroxides were dissolved with 2 mL of 37% (v/v) HCl. After pouring the sample into a beaker, the resulting solution was evaporated almost to dryness and the moist residue was then dissolved again using 2 mL of HCl 37% (3 times) and then evaporated each time until dryness. Lastly, the dried solutions were dissolved in 80 mL 2M HCl. Ascorbic acid (~ 0.1 g) was added at this stage to reduce iron (III) and eliminate its interference during the deposition process.

Each silver disc was plated at 85ºC for 3h while the plating solution was stirred continuously at ~600 rpm. At the end of the plating process, the disc was removed from the plating system, washed with distilled water and rinsed with acetone prior to the counting step with alpha spectrometry. The minimum detectable activity (MDA) obtained for ^{210}Po for liquid samples was 0.1 mBq/L.

Analytical method for solid samples

In a Teflon vessel, 200 mg of the dry sample was spiked with 0.5 mL of ^{209}Po (23.46 ± 0.80 Bq/L), to evaluate the radiochemical yield, and then 15 mL of HNO_3 were added. The vessel was then placed in the microwave oven set at a power of 900 W with an initial temperature of 50ºC. The temperature ramp was 10ºC/min up to 175ºC, at which point it was held for 30 minutes before the cooling down process. The total digestion time was 60 minutes.

To prevent losses of polonium after the microwave digestion, the vessels were immediately placed in the fridge for 24h to lower the temperature and pressure further. The sample digests were then filtered and transferred to beakers and evaporated nearly to dryness on a hot plate at 100ºC. The sample was dissolved in 80 mL of HCl 2M and then the autodeposition process was performed using the procedure described in the previous section. In this case, the minimum detectable activity (MDA) obtained for solid samples was 2 Bq/Kg.

Ingestion doses

Ingestion doses due to the consumption of mussels are calculated for adults using the following equation:

$$Ed_{\left(^{210}Po\right)} = A\left(^{210}Po\right) \cdot m \cdot C_f\left(^{210}Po\right)$$

where Ed (^{210}Po) (Sv) is the annual effective ingestion dose due to ^{210}Po ingestion, A (^{210}Po) is the ^{210}Po activity concentration (Bq/kg) in the mussel samples in fresh weight, m (Kg) is the estimation of annual intake of mussels (2 Kg of fresh mussel tissue per year per capita for coastal populations that traditionally consume mussels in their everyday diet) (Rozmaric et al. 2012; Aközcan 2013), and C_f (^{210}Po) is the dose coefficient for adults (1.2 x 10^{-6} Sv/Bq) (IAEA 2003).

Results and discussion

In order to get satisfactory results in the determination of ^{210}Po, it is necessary to assure good autodeposition of this isotope. In this respect, it should be mentioned that, in the literature, the different procedures designed for this purpose vary in terms of the experimental conditions used (Benedik et al., 2009; Díaz-Francés et al., 2013; Henricsson et al., 2011; Idoeta et al., 2011). With this in mind, in the first stage of our study, the effect of changing different parameters that can affect autodeposition were investigated. In particular, the plating solution was fixed in HCl 2M and the effect of changing the plating temperature and time was evaluated. We tested different values based on the existing literature, in particular, the deposition temperatures used in prior studies ranged from 60ºC to 95ºC, with the usual plating times being between 3 and 8 hours (Sánchez-Cabeza et al. 1997; Swift 1998; Benedik et al. 2009; Lin and Wu 2009; Casacuberta et al. 2010; Planisek et al. 2013).

The best results in terms of tracer recovery were obtained using a plating temperature of 85ºC over a period of 3 hours. Under these conditions, the recovery for ^{209}Po was 55 ± 5%. Moreover, it was observed that, when the time was increased, a slightly higher recovery was obtained (an increase of around 5%). However, in order to save time in the overall method, 3 hours was considered to be enough for the satisfactory autodeposition of ^{210}Po on the silver planchet.

For solid samples, the usual procedure for its digestion is by using an acidic microwave digestion. In our case we took 200 mg of sample and then it was transferred to a 100 mL Teflon vessel together with a volume of 15 mL of an acid and 0.5 mL of ^{209}Po (23.46 ± 0.80 Bq/L). Different acids that are commonly used in the literature have been tested for several authors such as HNO_3, HNO_3:HCl (3:1) and HNO_3:H_2O_2 (20:1) (Casacuberta et al. 2010; Din 2011; Henricsson et al. 2011; Planisek et al. 2013; Kilic et al. 2014; Marsico et al. 2014). This variability in terms of the acids used is mainly dependent on the kind of sample matrix which has to be analysed. For example, a number of authors have used HNO_3:H_2O_2 (20:1) for biological samples, such as mussels, fish, foodstuffs and chicken, as in this case the presence of hydrogen peroxide can be very useful for the oxidation of the organic compounds that are usually present in these kinds of samples (Casacuberta et al., 2010; Din, 2011; Marsico et al., 2014; Planisek et al., 2013).

In our case, for the sludge samples analysed, the best recoveries were obtained with the use of HNO_3 with a value of 45 ± 8%. However, for the other tested acids, the obtained recoveries were slightly lower, with values of 35 ± 5% and 40 ± 5%, for HNO_3:HCl (3:1) and HNO_3:H_2O_2 (20:1) respectively. Although the recovery values are slightly lower than some of the literature found in sediments and soils which were around 60%, the authors relate the values of the recovery at the composition of sample matrix which has been analysed.

Finally, to verify the digestion method, a sludge sample from Jeju Island (Republic of Korea) from an intercomparison exercise conducted in 2012 by International Atomic Energy Agency (IAEA) which contained 554 ± 19 Bq/kg of ^{210}Po was analysed under the optimal conditions obtained previously. The recovery value found in this case when we use the optimum conditions was 55 ± 5% and the measured activity for this isotope was 518 ± 33 Bq/kg, which is close to the certified activity value reported by the IAEA (Z-score value of -0.66). Z-score is calculated from the ratio between the difference of the reference value (provided by the intercomparison organizer) and the average experimental value obtained, and the standard deviation defined by the organizer of the intercomparison. The criteria established for this test, in terms of accuracy, has to be in the range between -2 and +2.

Drinking water treatment plant (DWTP)

As demonstrated in previous studies, drinking water treatment plants and the processes involved can concentrate the radioisotopes contained in the influent water in the sludge generated (Palomo et al. 2010b; Palomo et al. 2010c). Therefore, the radiological content of this sludge is directly related to the radiological quality of the influent water. In this respect, it can be stated that both the geology and the industrial activity related to this raw water play an important role. At this point, it should be noted the presence of a dicalcium phosphate plant located upstream of the DWTP in Flix (Tarragona, Spain). For several years, the plant conducted its activity without any environmental control and, as a result, one of the main problems it caused was releasing its waste streams into a reservoir of the Ebro River without any prior treatment, right up until the late nineties. In this regard, previous studies by our research group determined the presence of different natural isotopes from the ^{232}Th and ^{238}U series at high concentration activities in sludge samples taken in an area in front of the DCP plant (Mola et al. 2011).

Taking into account all of these previous results, influent and effluent water samples from the DWTP were analysed in this study for their ^{210}Po content. These samples were analysed using the procedure described in Section 2.4. The activities for ^{210}Po in the influent water samples analysed ranged between 0.2 and 1.28 mBq/l. However, in the case of effluent water samples, the values were below the minimum detectable activity (MDA) of 0.1 mBq/l in all cases. Taking into consideration the fact that some authors have verified that polonium has a strong affinity for suspended particles

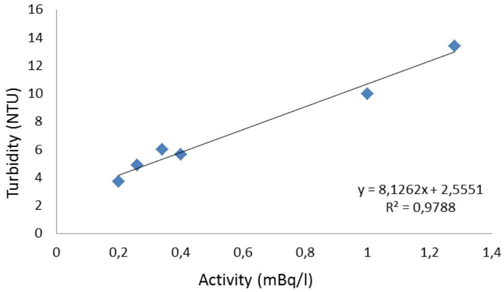

Fig. 2 Graph showing the relation between the measured activity for ^{210}Po and the turbidity of influent water samples from a DWTP.

present in water and so ^{210}Po activity is more associated with the particulate phase (Idoeta et al. 2011; Mohamed et al. 2013), it was also verified whether the measured activity in the water samples analysed is dependent on the turbidity of these samples. Figure 2 shows that there is a clear correlation between both parameters, thus confirming the affinity of polonium for the particulate matter. With the obtained activity results of the influent and effluent water samples analysed, a decrease in the ^{210}Po activity could be observed due to the processes applied in the DWTP. Consequently, it can be confirmed that the generated sludge samples concentrate these isotopes. Thus, different sludge samples taken at different periods of time were analysed. The values obtained are shown in Table 1, along with the corresponding uncertainty values and the recovery of the tracer obtained in each case.

From the results obtained, it can be observed that the maximum concentrations of ^{210}Po were found in December 2014 (42 ± 4 Bq/kg for dry weight). However, this value is not significantly different from the other months analysed. Moreover, an important consideration is that, according to the relationship between the amount of influent water and the sludge generated (1m^3 water generates 15 g of sludge (internal calculation from the DWTP)) and the measured activity of ^{210}Po for the sludge samples, the corresponding activity value for the river water can be estimated. In our case, the mean activity value of ^{210}Po in the sludge was 37 ± 5 Bq/kg and, applying the above mentioned ratio, it can be estimated that the ^{210}Po content in the river water would be around 0.56 mBq/l. This value is comparable with the mean value of 0.74 ± 0.23 mBq/l measured in the influent water samples. So, in short, an important point highlighted by our work is that it is possible to estimate the ^{210}Po activity concentration in the raw water samples of the DWTP from the activity measured in the sludge samples. Regarding the obtained activity values for ^{210}Po in the sludge samples and knowing the activity of ^{226}Ra (around 20 Bq/Kg), it is worth to mention that through these values it is not possible to establish a correlation with the DCP activity since our values are comparable to the activities expected in normal

Table 1. Activity concentration and uncertainty of ^{210}Po in different analysed sludge samples from the DWTP of L'Ampolla (Tarragona, Spain).

Sample		Alpha Spectrometry	
		% Recovery	^{210}Po (Bq/kg) (dw)^{a}
DWTP	Nov ’14	54 ± 2	39 ± 3
	Dec’14	49± 7	42 ± 4
	Jan’15	36 ± 1	36 ± 3
	Feb’15	36 ± 3	31 ± 1

^{a} Mean value for 3 replicates.

soil, according to UNSCEAR (2008) the average of ^{226}Ra activity concentration worldwide is 32 Bq/Kg, and presumably ^{210}Po will be similar in the radioactive equilibrium (or higher due to excess ^{210}Pb contribution from the atmosphere).

Biological samples

It is well known that marine biota is capable of concentrating various toxic elements, such as radionuclides, within their tissues (Aközcan 2013; Mola et al. 2013). In this respect, different species were considered in this study for measuring the ^{210}Po activity. In particular, three type of fish samples from Ebro river were analysed, as well as mussels (collected from sea in front of Ebro river) and also apple snails which is a recently introduced invasive species in the Ebro river area. In the case of mussels it should be highlighted that mussels are an important element of the human diet that are commonly used for pollution monitoring due to their sedentary, filter-feeding habits and the ease of using them for sampling purposes (Aközcan 2013).

The applied approach was the method previously optimized for sludge samples and the first step was to compare the recoveries obtained for this type of biota samples with the recoveries previously obtained for sludge samples. The recoveries were found to be between 31% and 53%. They are therefore comparable with the values previously recorded for the other

Table 2. Activity concentration and uncertainty of ^{210} Po (Bq/kg) in dry weight (dw) in different biological samples (muscle tissues in fish and soft parts in shellfish).

Sample		Alpha Spectrometry	
		% Recovery	^{210}Po (Bq/kg) (dw)[a]
Muscle of Catfish *(Silurus glanis)*		41 ± 1	<MDA
Muscle of Perch *(Perca fluviatilis)*		51 ± 2	<MDA
Muscle of Carp *(Cyprinus carpio)*		49 ± 2	<MDA
Muscle of Apple snail (*Pomacea bridgesii)*		35 ± 5	164 ± 37
Mussel (Ebro River)	Alfacs bay	34 ± 13	271 ± 50
(Mytilus edulis)	Alfacs bay commercial	31 ± 7	341 ± 35
	Fangar bay	36 ± 6	366 ± 10
Mussel (Galicia) *(Mytilus edulis)*		53 ± 4	204 ± 1

[a] Mean value for 3 replicates.

samples analysed (Table 1 and 2) and the values from other authors, despite the differences in the matrix composition so it is important to highlight that in our case the developed method is applicable for both types of matrices.

Regarding the fish samples, three different types of fish were collected, including catfish, perch and carp. The fish samples were cleaned and only the comestible part (muscle) was analysed immediately after the collection. The activities recorded for all of the fish samples were lower than the MDA which was 2 Bq/kg. With respect to the literature regarding the determination of ^{210}Po in different fish species, in the case of the muscle, the measured activity ranged between 2 and 6 Bq/kg which are in accordance with our found values. It is important to highlight that other researchers have demonstrated that the highest average activities of this isotope in fish from commercial fishing boats were observed in the organs of the digestive system, especially in the intestines, liver and stomach (Carvalho 2011; Marsico et al. 2014).

Another interesting species to consider is the apple snail, a recently introduced invasive species in Ebro river. These organisms inhabit a wide range of ecosystems from swamps, ditches and ponds to lakes and rivers. They are some of the largest freshwater snails and they consume vast amounts of rice and can devastate the flora and fauna of natural wetlands. A number of apple snail were analysed to verify if these organisms are capable of concentrating the polonium present in the Ebro River. To do so, ten specimens with a media length of 5.5 cm were collected and the soft parts were separated from the shell before being analysed for their ^{210}Po content. The activity recorded for the isotope in muscle part was 164 ± 37 Bq/kg. Even though, these values cannot be compared because there are no studies in the literature in this type of animals but the values obtained are lower than the other species analysed.

Mussels have been demonstrated to be bioaccumulators because of their ability to concentrate several environmental contaminants in their tissues (Mola et al. 2013). In our case, blue mussels were studied and they were collected at the mouth of the river in the bays of Fangar and Alfacs by the *Institut de Recerca i Tecnologia Agroalimentàries* (IRTA) (Figure 1). Activity concentrations of ^{210}Po in mussel samples were 366 ± 10 Bq/kg (dw) and 271 ± 50 Bq/kg (dw) for Fangar Bay and Alfacs Bay (Table 2), respectively. Moreover, mussels collected in Alfacs Bay were also purchased in a local market to ascertain if there were any changes in the activity concentration of ^{210}Po due to the purification process that these mussels undergo before sale. The activity found in the commercial mussels and mussels collected directly from Alfacs Bay were not significantly different considering their uncertainties. Additionally, mussels from another region of Spain (namely north-western Spain in the area of Galicia, on the Atlantic coast) were analysed to see if any differences were noted due to the different water with which they are in contact. The activity concentration found in this case was 204 ± 1 Bq/kg, lower than the activities found in mussels from the Ebro Delta area. One possible reason to explain such differences can be attributed to the presence of the DCP upstream of the river course, but to confirm that a comparison with other values previously found in the literature was performed. in this regard it is important to mention that a great variability can be observed in the results that different authors have obtained that range between 4 and 1470 Bq/kg (dw) as it is shown in Table 3. In general, based on these studies, it can be concluded that, when different industrial activities such as iron and steel factories, fuel storage yards, fertilizer factories, and natural gas power plant, among others, are located in the area of influence from which the mussel samples are taken, higher activity values are obtained. Examples include a study by Aközcan et al. (2013) in which they collected

Table 3. Total annual ingestion doses (µSv/y) in different regions around the world due to activity concentration of ^{210}Po derived from mussel ingestion.

Area	^{210}Po (Bq/kg dw)	^{210}Po (µSv/y)[a]	References
Portugal	132	63	(Carvalho 2011)
Turkish Sea cost, Turkey	26-280	12-134	(Kilic et al. 2014)
Slovenian and Italian coast in the Gulf of Trieste	222-399	107-192	(Kristan et al. 2015)
Japan	300-353	144-169	(Baumann et al. 2013)
Portugal	460-1470	221-706	(Carvalho et al. 2011)
Slovenia	3,8-367	2-176	(Planisek et al. 2013)
Candarli Gulf, Turkey	332-776	159-372	(Aközcan 2013)
Alfacs and Fangar Bay, Spain	271-366	130-175	Present study
Galicia, Spain	204	98	Present study

[a] Ratio fresh weight / dry weight = 5.

samples in the eastern Aegean Sea (Turkey), in an area that it has been strongly affected by growing population and industria-lization. There are iron and steel factories, fuel storage yards, fertilizer factories, natural gas power plant, electrical substations and other medium and small establishments in the region where mussels were obtained. Major industrial developments located in the coastal area had been discharging solid and liquid wastes into the sea after minimal treatment. In this case, the values found for polonium activity ranged between 332 and 776 Bq/kg. In that study, the authors concluded that the difference between the activity concentration of ^{210}Po and ^{210}Pb can also indicate that obtained ^{210}Po activity concentrations in the mussel samples do not only occur from the natural origin. Therefore, based on the obtained results, it can be concluded that the presence of the DCP factory a few kilometres upstream of the bay of the Ebro River where the mussels were collected could aid to increase slightly the activity of polonium present in the analysed samples.

Ingestion doses due to shellfish consumption

^{210}Po in the marine environment exists in significant amounts and constitutes the main dose contributor of all of the natural radionuclides, due to the consumption of marine foodstuffs (Kilic et al. 2014).

The annual effective ingestion dose was calculated for mussels with the equation indicated previously (Section 2.5). The value of the committed effective dose depends on the radionuclide under consideration and on the age of the population. In this study, the annual committed effective dose of ^{210}Po for adults (>17 years) by the ingestion of mussels has been determined, under the assumption of a consumption of 2 Kg of mussels per year per capita (Rozmaric et al. 2012; Aközcan 2013). The activity concentration in the calculation of annual ingestion doses must be expressed in terms of fresh weight and, as such, the ratio between fresh weight (fw) and dry weight (dw) (fw/dw = 5) was taken from the study by Rozmaric *et al*. (2012) which agrees to the ratio obtained for the samples included of this study. Table 3 shows the values of the annual effective ingestion doses calculated for the different studies reported in the literature, as well as for this study. The values obtained ranged between 130 and 175 µSv/y (Carvalho et al. 2011; Carvalho 2011; Aközcan 2013; Baumann et al. 2013; Planisek et al. 2013; Kilic et al. 2014; Kristan et al. 2015).

In short, the annual effective dose found for the mussels analysed in our study is comparable with other values estimated in different regions around the world with low industrial activity (Table 3). However, in the case of other studies in the literature, the estimated values were considerably higher and this may be related to the presence of other industrial activities along the coast as for example in the case of two studies in which mussels from two different geographical areas were analysed, in particular from Costa da Caparica in Portugal where is not affected by direct waste discharged is located and in this case the calculated dose reached values of 706 µSv/y and on the other hand an study located in in the Candarli Gulf in Turkey where there are industrial affectation but neither affected by direct waste discharged with values that reached the annual effective dose of ^{210}Po of 372 µSv/y.

In our case, the obtained ingestion dose in the case of the mussels taken from Ebro delta area were higher than the obtained values for the mussels of another region of Spain (Galicia) and one possible reason of such behaviour is the presence of the DCP industry which can contribute to an increase of the ^{210}Po activity.

Conclusions

In the analysed samples from the DWTP, ^{210}Po could be detected in influent water at levels of low mBq/l (between 0.2 and 1.28 mBq/l), with activities in effluent water being below MDA (0.1 mBq/l). In contrast, in the sludge from the DWTP, ^{210}Po activities were found in the range of 31 to 42 Bq/kg, so these results confirm that due to the water treatment process followed in this plant, a concentration of this isotope takes place. However, the obtained activity values are quite comparable to the ^{210}Pb activities expected in normal soil, according to UNSCEAR (2008). Furthermore, using the activities found in the sludge and the relation between influent water and sludge produced by the DWTP, it was possible to estimate the activities in influent water.

Fish and shellfish, such as mussels, were analysed in order to ascertain to what extent of the effect of the industrial activity on the organisms present in the Ebro River. In fish samples, the activities were below 2 Bq/Kg. However, in the case of mussels, the activities recorded were between 271 and 366 Bq/kg (dw), in line with other studies reported in the literature. By comparing with other mussels from another region of Spain (Galicia, on the Atlantic coast), it can be seen that the activity concentration found in the mussels from the bay of the Ebro River could be slightly affected by the industrial activity in the river. Lastly, ingestion doses were calculated for all of the mussel samples and the highest result found for an adult was 175 µSv/y, which is below the range published by the UNSCEAR (2008) and in the levels obtained in bibliography in areas with low industrial activities.

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3.1.3. Discussió de resultats

A continuació es discuteixen els resultats més importants dels treballs realitzats en aquest primer bloc, en els que s'han determinat diferents radionúclids (naturals i artificials) en mostres ambientals derivades de la industrialització al tram baix del riu Ebre.

En el primer estudi, es van optimitzar diferents paràmetres per tal de millorar l'eficiència de comptatge per a la mesura dels isòtops de ^{55}Fe i ^{63}Ni mitjançant un detector d'escintil·lació líquida. Es van provar diferents volums del medi d'elució del ^{55}Fe i ^{63}Ni de la columna, així com també diferents líquids d'escintil·lació. Els valors òptims van ser 1 ml de mostra i 19 ml *d'Optiphase Hisafe 3*, com a líquid d'escintil·lació per al ^{55}Fe i 4 ml de mostra i 16 ml *d'Optiphase Hisafe 3* per al ^{63}Ni. L'eficiència de comptatge per a la mesura del ^{55}Fe i ^{63}Ni va ser 22 ± 2 % i 55 ± 5 %, respectivament, essent aquests valors comparables amb els valors trobats a la bibliografia per aquests emissors beta [1–4].

El següent pas, va ser la validació del mètode mitjançant l'anàlisi d'una mostra de sòl (composta per 70% de carbonats amb baix nivell de ^{55}Fe i ^{63}Ni) procedent d'un exercici d'intercomparació organitzat pel Consell de Seguretat Nuclear (CSN). Aquest òrgan utilitza el test Z-score com a paràmetre per validar els diferents mètodes emprats per a la determinació d'aquests radionúclids, establint com a criteri valors acceptables de Z, ± 2. En el nostre cas, s'ha validat el mètode satisfactòriament amb una Z-score = -1.7 i 0.1 pel ^{55}Fe i ^{63}Ni , respectivament.

Quan el mètode va ser aplicat per a la determinació de ^{55}Fe i ^{63}Ni en mostres de sòls de l'ETAP, es va trobar la problemàtica d'unes interferències provocades per la quimioluminescència que dificultava una correcta quantificació del contingut de ^{55}Fe en la mostra. Aquest mateix fenomen es va poder veure en un estudi anterior, concretament al de Geckeis i col. [5] on es va relacionar la quantitat d'interferència amb la quantitat i tipus de mostra utilitzada. En l'estudi de Geckeis i col., la interferència en la mesura del ^{55}Fe apareixia quan la matriu presentava concentracions de Fe(III) elevades. En el nostre cas, té una certa relació perquè en una de les etapes de potabilització d'aigua, s'utilitza $FeCl_3$ com a coagulant, per tant, les concentracions de ferro estable en els fangs estudiats són elevades (entre 100 i 120 mg/L).

Per tal de confirmar que els problemes d'interferències en l'espectre del ^{55}Fe són deguts a l'alta concentració de ferro estable a la matriu, es va fer una prova amb l'addició diferents quantitats de $FeCl_3$ (1 - 5 mg). En els resultats, es va poder corroborar la procedència de la interferència, ja que com més elevada era la concentració de ferro estable, més comptes es podien veure en el pic interferent de l'espectre.

Amb una síntesi bibliogràfica exhaustiva, es va veure que l'alt contingut de $FeCl_3$ que provoca la interferència en l'espectre del ferro, es degut a una reacció de quimioluminescència. Per tal disminuir l'energia d'activació i així finalitzar la reacció més ràpidament, es va optimitzar la temperatura d'emmagatzematge de la mostra. Es van preparar cinc vials amb mostra de referència i després de fer una primera mesura, es van emmagatzemar cadascun dels vials a una temperatura diferent (6, 20, 40, 60 i 80 ºC) durant 8 hores. A continuació es van mesurar i després es van tornar a emmagatzemar durant 8 hores (es va repetir aquest procediment 3 cops més). Com a resultat, es va poder veure que com més alta era la temperatura més ràpid decreixia el pic de la interferència, i conseqüentment es podia mesurar més aviat. No obstant, en el cas de temperatures elevades (sobre els 80ºC), es va veure que el líquid d'escintil·lació no era totalment estable. Així doncs, tenint en compte tots els resultats, es va considerar que el millor era deixar les mostres una setmana a temperatura ambient abans de mesurar-les.

Un cop resolta la problemàtica, es va analitzar el contingut de ^{55}Fe i ^{63}Ni en les mostres de fangs de l'ETAP. Es van analitzar mostres de tres mesos diferents, les activitats obtingudes pel ^{55}Fe va ser de <15 a 162 Bq/kg, mentre que el ^{63}Ni va ser de <10 a 65 Bq/Kg. Amb aquests valors, i sabent que amb cada 1 m^3 d'aigua superficial d'entrada a la planta es generen 15 g de fangs, es va poder fer una estimació de les activitats de ^{55}Fe i ^{63}Ni que hi ha a l'aigua del riu. Amb aquesta estimació es podrà evitar fer els anàlisis d'aquests isòtops en les mostres d'aigua de riu, estalviant temps ja que els mètodes són força llargs i tediosos (requereixen molt volum de mostra).

El següent estudi d'aquest bloc, se va centrar en determinar el ^{210}Po en mostres d'aigua d'entrada i sortida i de fangs generats a l'ETAP, així com també en mostres de biota. D'una banda, l'interès d'aquestes mostres recau en verificar la influència de les indústries NORM i d'altra banda en veure l'efecte que tenen sobre la població que en consumeix.

El primer pas va ser l'optimització del mètode. Pel que fa a les mostres sòlides, es va fer una optimització del procediment de digestió de la mostra amb els diferents àcids més utilitzats a la bibliografia (HNO_3, HNO_3/HCl (3:1) i HNO_3/H_2O_2 (20:1)) [8,10–13]. En el nostre cas, tant per a les mostres de fangs com per a les biològiques el millor àcid per fer la digestió va ser el HNO_3.

Seguidament, donada l'elevada variabilitat de les condicions d'auto-deposició reportades a la bibliografia [6–9], es va creure necessari optimitzar el procediment d'auto-deposició del ^{210}Po en planxetes de plata. Els diferents paràmetres que afecten a l'auto-deposició són la concentració d'àcid al medi, el temps i la temperatura d'auto-deposició. Després de fer les proves pertinents, les condicions òptimes finals en aquest estudi van ser: una concentració d'HCl 2 M, 85 ºC i 3 hores. En aquestes condicions el rendiment va ser de 55 ± 5%.

Finalment, per tal de validar el mètode, es va analitzar una mostra d'intercomparació de la IAEA *(International Atomic Energy Agency)* com a mostra de referència, obtenint resultats satisfactoris (Z-score = -0.66). Finalment, el mètode optimitzat i validat va ser aplicat a la determinació de ^{210}Po en mostres d'aigua d'entrada i sortida de la planta, fangs i mostres de biota.

Els resultats obtinguts en les mostres d'aigua superficial d'entrada van ser entre 0.2 i 1.28 mBq/L mentre que en les de sortida l'activitat va ser inferior a l'activitat mínima detectable (AMD) que és 0.1 mBq/L. En canvi, en les mostres de fangs es van poder veure activitats des de 31 a 42 Bq/Kg. Així doncs, amb aquests resultats es va poder confirmar que durant els processos de potabilització de l'aigua es concentren els radionúclids als fangs.

Igual que en l'estudi anterior, es va fer una estimació utilitzant la relació entre la quantitat d'aigua d'entrada i el fangs generats (1 m^3 d'aigua generen 15 g de fangs). Així doncs, amb la mitjana de l'activitat dels fangs (37 ± 5 Bq/kg) obtindríem una activitat a l'aigua de 0.56 mBq/L. Aquest valor estimat és comparable al valor mitja obtingut, 0.74 ± 0.23 mBq/L. Per tant, en aquest treball es va confirmar que amb les activitats obtingudes en els fangs es pot estimar l'activitat de l'aigua superficial d'entrada, evitant tenir que analitzar grans quantitats d'aigua (4L).

Amb les activitats de ^{210}Po obtingudes, no es va poder establir una correlació amb la presència de la indústria de fosfat bicàlcic, donat que d'acord amb la UNSCEAR [14] el valor mitjà d'un sòl estàndard és de 32 Bq/Kg de ^{226}Ra i assumint l'equilibri secular també ho serà de ^{210}Po.

Respecte a les mostres biològiques, es van escollir tres tipus de peix (silur, perca i carpa), una espècie invasora (el cargol poma) procedents del riu Ebre i musclos procedents de les dues badies properes a la desembocadura del riu Ebre. Els resultats obtinguts en tota la part comestible dels peixos, van estar en concordança amb resultats de la bibliografia respecte zones no afectades per la indústria [13,15], per sota l'activitat mínima detectable (2 Bq/kg). Pel que fa als cargols poma, es va dur a terme l'anàlisi per veure si aquestes espècies tenien la capacitat de concentrar radionúclids a l'interior del seu organisme. Tot i obtenir uns resultats força elevats (164 ± 37 Bq/Kg), no es van poder comparar amb cap estudi ja que no hi ha dades a la bibliografia, tot i això aquests organismes presenten activitats més elevades que a l'aigua per tant podem veure una certa concentració a l'interior del seu organisme. Per acabar es van analitzar mostres de musclos, en les que es van obtenir activitats de ^{210}Po de 366 ± 10 Bq/kg i 271 ± 50 Bq/kg (pes sec) per a les dues badies de la desembocadura del riu, Fangar i Alfacs, respectivament. Per tal de comparar aquests valors, es va analitzar una mostra procedent d'una altra regió de la península, concretament de Galícia. En aquest cas els resultats van ser de 204 ± 1 Bq/kg (valors per sota de les activitats obtingudes a les mostres de la desembocadura del riu Ebre). Aquestes diferències poden ser atribuïdes a la presència de la indústria de fosfat bicàlcic aigües amunt del riu Ebre.

Finalment, es va fer una estimació de les dosis per ingesta de musclos en la dieta tenint en compte que tota l'activitat que presenten els musclos es absorbida per l'organisme. Els valors obtinguts varien entre 130 i 175 µSv/any, el quals tenen una toxicitat comparable a altres estudis que analitzen musclos amb zones en baixa activitat industrial, donat que les dosis depenen de la quantitat de cada mol·lusc que se'n consumeix a cada país [12,16–18].

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3.2. Determinació de radionúclids en mol·luscs del delta de l'Ebre

Arran dels resultats obtinguts en els treballs anteriors, en els què s'ha observat la presència de radionúclids d'origen natural en elevades concentracions, concretament de ^{210}Po en mostres de biota, es va plantejar aquest estudi. L'objectiu principal és avaluar el contingut de radionúclids naturals (^{210}Po, ^{210}Pb, ^{234}U, ^{238}U, ^{232}Th i ^{230}Th) en totes les espècies de mol·luscs (navalles, ostrons, cloïsses i musclos) que es produeixen al delta de l'Ebre. També és objectiu d'aquest estudi, estimar la dosi efectiva a la que el públic consumidor d'aquestes espècies està exposat.

Altres estudis existents a la bibliografia, on s'analitzen mol·luscs, han posat en manifest que són organismes filtradors, ja que s'alimenten del fitoplàncton per mitjà de la filtració d'aigua a través de les brànquies [1–4]. A més a més, en alguns d'aquests estudis s'ha pogut veure que aquests organismes tenen la capacitat d'acumular i concentrar molts dels contaminants així com també radionúclids que hi ha presents al medi on viuen [5,6]. Per això, s'han utilitzat aquests organismes, per determinar les concentracions d'activitat de diferents radionúclids de la zona on resideixen. Cal destacar, que en alguns d'ells s'ha pogut veure una relació entre l'activitat mesurada i certs paràmetres, com els canvis estacionals i l'activitat industrial [6–11]. Per exemple, els estudis de Aközcan i Strok and Smodis [9,10] mostren diferències en l'activitat del ^{210}Po i ^{210}Pb entre les diferents estacions meteorològiques. Els autors atribueixen aquestes variacions al cicle biològic en que estan els mol·luscs i també mencionen l'efecte de les condicions ambientals (a altes temperatures els mol·luscs bioacumulen menys ^{210}Po degut a la disminució del consum de fitoplàncton). A més, altres estudis han relacionat les altes activitats de radionúclids naturals (^{238}U, ^{232}Th, ^{210}Po i ^{210}Pb) amb la presència d'activitats industrials tals com indústries de fertilitzants o indústries d'àcid fosfòric, entre d'altres [12].

Com ja s'ha comentat anteriorment, la indústria de fosfat bicàlcic, localitzada en el tram final del riu Ebre, pot aportar un augment de radionúclids naturals al medi. Tot i tenir la zona de la indústria en procés de descontaminació, poden haver també sediments contaminats al llarg de tot el riu, que poden afectar als organismes vius que viuen en aquestes aigües.

A partir de les dades observades en aquests estudis i tenint en compte l'elevada producció de mol·luscs al delta de l'Ebre, es va plantejar un estudi per caracteritzar radiològicament els mol·luscs que es produeixen a la badia del Fangar (ubicada al delta de l'Ebre). Les mostres seleccionades van ser navalles, ostrons, cloïsses i musclos. A més a més, es va agafar una altra espècie, concretament el cargol de mar, com a espècie de referència, donat que no es cultiva a la badia i que per tant, no està en contacte amb els sediments del riu Ebre.

Atès que en alguns estudis es va poder veure una certa variació de les activitats dels radionúclids depenent de l'estació meteorològica, es va realitzar el mostreig en dues estacions diferents (estiu i hivern).

Seguidament a aquesta breu introducció, s'inclou l'article resultant d'aquest estudi on es presenten i es discuteixen els resultats obtinguts, en aquest cas, està pendent de la seva acceptació i publicació a la revista *Journal of Environmental Science and Pollution Research.*

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3.2.1. Bioaccumulation of natural radionuclides in molluscs from Ebro Delta

BIOACCUMULATION OF NATURAL RADIONUCLIDES IN MOLLUSCS FROM THE EBRO DELTA AREA

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Abstract

^{210}Po, ^{210}Pb, ^{234}U, ^{238}U, ^{232}Th and ^{230}Th were analysed in the edible part of four different species of bivalves typically produced and consumed in the Ebro Delta area. The results show that the main contributor to the radioactive content in these species was ^{210}Po, with values ranging between 263 and 813 Bq/Kg (d.w.), which are higher than the usual reported activity levels in other geographical areas. This can probably be attributed to the activities of a phosphate industrial plant located upstream on the River Ebro, which may lead to enhanced levels of naturally occurring radioactive isotopes in the aquatic ecosystem. To determine the possible impact on health, the committed effective doses through the consumption of the different species were evaluated and the values varied from 1.50 to 149.61 μSv y^{-1}, which is in the range of (200 – 1000) μSv/y given by UNSCEAR.

Keywords: natural radionuclides, molluscs, annual ingestion doses

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Environ. Sci. Pollut. Res., submitted

Introduction

The mollusc group feeds on phytoplankton by pumping water across their gills. Consequently, they have the ability to accumulate and concentrate most contaminants at much higher levels than those found in the water in which they live. For this reason, molluscs, and especially bivalves, have commonly been used to determine the levels of different contaminants, such as natural radionuclides, in the marine environment, since they can be representative of the water quality (Stepnowski and Skwarzec 2000; Carvalho 2011; Feroz Khan et al. 2011; Khan and Wesley 2012; Kilic et al. 2014; Uddin and Bebhehani 2014).

There are several studies that focus on the determination of these natural radioisotopes in molluscs from different regions around the world, although most of them focus on mussels. Based on these studies, although there is no homogeneity in the results obtained in terms of the levels of activity concentration, some authors conclude that there is a relationship between the measured activity and certain parameters, such as seasonal changes or industrial activities (Boisson et al. 2001; Connan et al. 2007; Carvalho et al. 2011; Strok and Smodiš 2011; Rozmaric et al. 2012; Musthafa and Krishnamoorthy 2012; Aközcan 2013; Kilic et al. 2014; Uddin and Bebhehani 2014; Bode et al. 2015; Krmpotić et al. 2015). For example, Strok and Smodiš (Strok and Smodiš 2011) and Aközcan (Aközcan 2013) reported large activity concentration variations in ^{210}Po and ^{210}Pb in molluscs between different seasons and attributed these differences to the different biological cycles of the evaluated molluscs depending on the season. Moreover, some of these studies showed high levels of ^{238}U, ^{232}Th, ^{210}Po and ^{210}Pb in molluscs due to industrial activity involving naturally occurring radioactive materials (NORM). For example, it is worth mentioning the study by Krmpotić *et al.* (Krmpotić et al. 2015), whose work focused on an area close to uranium mining and milling activities, phosphoric acid industries and phosphate fertilizers. As a result of their research, the authors concluded that the activities recorded may present enhanced values of the measured isotopes on account of the proximity to those industrial areas.

Considering that, in previously published papers, certain authors have emphasized the relation between the radiological content in these species and the presence of industries, our study focuses on an area with a great tradition of bivalve cultivation for human consumption, the Ebro Delta (Catalonia, NE Spain). In this area, the annual production is over 4,000 tonnes of mussels, 800 tonnes of large oysters and 30 tonnes of clams. The interest in this area is due to the possible affectation of NORM industries, in particular the dicalcium phosphate plant (DCP) operating a few kilometres upstream on the Ebro River, in Flix (Catalonia, Spain), which ends at the mouth of the Delta. For a number of decades, this plant dumped several tonnes of industrial waste into a reservoir located nearby. Although, nowadays, the area is treated, there are also accumulated contaminated sediments along the banks of the Ebro River which may affect the aquatic organisms present in the area (Mola et al. 2013a).

With all of this in mind, this study was designed in order to gain accurate knowledge of the activity concentration of different natural isotopes (^{210}Po, ^{210}Pb, ^{234}U, ^{238}U, ^{232}Th and ^{230}Th) on various species (razor shells, large oysters, mussels, clams and sea snails) cultivated and consumed in the Ebro Delta area, also taking possible seasonal variations into consideration. In addition, another important aim was to estimate the annual dose to which the public is exposed in terms of health and safety.

Materials and methods

Sampling

The different molluscs included in this study were collected in winter (January to March) and summer (July), provided by the local fishermen in Fangar Bay (Ebro Delta) which is shown in Figure 1. In particular, different bivalves were collected that are usually consumed in this area: razor shells (*Ensis arcuatus,* n = 50), large oysters (C*rassostrea gigas,* n = 20), mussels (*Mytilus galloprovincialis,* n = 120) and clams (R*uditapes philippinarum,* n=250). In addition, a reference sample was also taken into consideration, namely the sea snail (*Murex brandaris*, n = 100), sampled in the rocks which are outside the bay. Once in the laboratory, the samples were washed thoroughly with distilled water to free them from attached sand/silt, due to high radionuclide association with silt/detritus materials. Then, the soft tissue was separated and dried in an oven at 80ºC (to prevent polonium loss) overnight to constant weight and homogenized. The samples were then crushed and sifted in a 250 µm sieve. After measuring polonium levels, about 10 g of dry sample were introduced in a muffle furnace at 550ºC for 12 hours in order to destroy all of

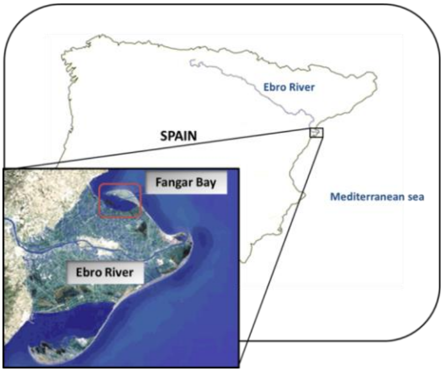

Fig.1. Sampling location in Ebro Delta (NE Catalonia, Spain).

the organic matter before the determination of the rest of the radionuclides.

Methods

Radiochemical separation of uranium and thorium isotopes

The method used to determine the uranium isotopes (^{234}U and ^{238}U) and thorium isotopes (^{232}Th and ^{230}Th) was described in a previous study by Mola *et al.* (Mola et al. 2013b).

The first step was the digestion of the calcined sample with a microwave oven. In a Teflon vessel, 300 mg of sample was spiked with a ^{232}U and ^{229}Th certified solutions with an activity concentration of (15.01 ± 0.15) Bq/g and (20.91 ± 0.29) Bq/g, respectively, and then 15 mL of HNO_3 (65%) was added. The vessel was then placed in the microwave oven set at a power of 900 W with an initial temperature of 50 ºC. The temperature ramp was 10 ºC/min up to 175 ºC, at which point it was held for 30 min before the cooling process. The total digestion time was 60 min.

After the digestion of the sample, this method consisted of the separation of the uranium and thorium isotopes using an UTEVA resin (Eichrom, Bruz, France). Then, uranium and thorium solutions were evaporated to dryness, re-dissolved and transferred to an electrodeposition cell and the isotopes were electrodeposited in a stainless steel planchets (diameter 25.15 mm and thickness 0.6 mm) for 2 hours, under a current density of 1.5 A/cm^2 and subsequently measured by alpha-spectrometry.

Radiochemical separation of ^{210}Po isotopes

The method used to determine ^{210}Po was described in a previous study by Fonollosa *et al*. (Fonollosa et al. 2015). Briefly, the dried samples were spiked with a ^{209}Po certified solution with an activity concentration of (23.46 ± 0.80) Bq/L, and then digested in the same conditions as the uranium and thorium separation method. Digested samples were filtered (0.45 µM filter), transferred to beakers and evaporated almost to dryness on a hot plate at 80 ºC. Then, the samples were dissolved in 80 mL of 2M HCl and then the autodeposition process was performed for 3 hours at 80 ºC using silver planchets (diameter 25.15 mm and thickness 0.6 mm) and subsequently measured by alpha-spectrometry.

Radiochemical separation of ^{210}Pb isotopes

To determine ^{210}Pb, a method described by Mola *et al*. (Mola et al. 2014) was used. As in the other methods, the first step was the digestion of the calcined sample with the same conditions mentioned above. This method was based on an isolation and pre-concentration of ^{90}Sr and ^{210}Pb using an Sr-resin. The lead fraction was collected directly in a separated 20 mL polyethylene (PE) liquid scintillation vial and mixed with 16 mL of scintillation cocktail.

Instrumentation

A speedwave four microwave digestion system with built-in, non-contact temperature and pressure measurement, supplied by Berghof (Eningen, Germany), was used for the digestion of samples. Twelve pressure vessels made of a fluoropolymer were located in a rotor with a gas collection system in which 1,450 W of microwave power can be obtained.

LOV-MSFIA (Lab On Valve – Multi-Syringe Flow Ingestion Analysis) system was used for the selective separation of ^{210}Pb (Mola et al., 2014). It has different integrated parts: a multi-syringe burette (BU4S; Crison Instruments, Barcelona, Spain) equipped with a 10 mL syringe (S1) (Hamilton, Switzerland) which were used as liquid driver and reservoir of internal standards, a LOV microconduit (Sciware Systems, Palma de Mallorca, Spain) encompassing eight peripheral integrated micro-channels (1.5 mm i.d.. 16.0 mm length, enclosing the bead column channel) installed on top of an eight port multi-position selection valve (Crison Instruments, Barcelona, Spain) and connected through the central port to S1 via a holding coil (HC). An external solenoid commutation valve (MTV-3-N 1/4 UKG; Takasago, Japan) was connected to the peripheral port 2 of the LOV in order to direct the flow as desired (on: in-line flow towards the autosampler; off: to waste). The system was automatically controlled by the software package AutoAnalysis 5.0 (Sciware Systems).

An alpha-spectrometer was used to determine the individual isotopes of uranium (^{238}U and ^{234}U), thorium (^{230}Th, ^{232}Th) and polonium (^{210}Po). The alpha-spectrometer (EG&G ORTEC, Model 676A, Oak Ridge, Tennessee) includes an ion-implanted silicon detector (ORTEC, size: 450 mm^2; alpha resolution: 25 keV FWHM at 5.48 MeV of ^{241}Am) in a vacuum chamber (Edwards Model E2M8, Sanborn, New York), a detector bias supplier, a preamplifier, a linear amplifier and a multichannel pulse height analyser with Maestro for windows software. Throughout the measurement, the pressure of the chamber was maintained at 1.06 kPa (7.95Torr).

^{210}Pb was determined by an ultra-low level liquid scintillating counting (LSC) in a Quantulus 1220^{TM} from Perkin-Elmer (Turku, Finland) with WinQ and Easy View software.

Annual ingestion doses

Ingestion doses due to the consumption of molluscs were calculated for adults using the following equation (Rozmaric et al. 2012; Aközcan 2013):

$$Ed = A \cdot m \cdot C_f$$

where *E*d (Sv) is the annual effective ingestion dose due of each radionuclide, *A* is the activity concentration of each radionuclide (Bq/kg) in the molluscs samples in fresh weight, *m* (kg) is the estimation of annual intake each of mollusc species (0.04 kg of fresh razor shell, 0.01 kg of large oyster, 0.17 kg of sea snail, 0.64 kg of clam and 1.15 kg of mussels of fresh tissue per year per capita for coastal populations that traditionally consume molluscs in their everyday diet) (AESSAN (Agencia Española de Seguridad Alimentaria y Nutrición; Ministerio de Sanidad; Servicios Sociales e Igualdad) 2011) and C_f is the dose coefficient for adults (Sv/Bq), available from the IAEA report (IAEA 2003). The values of the dose coefficient used for ^{210}Po, ^{210}Pb, ^{234}U and ^{238}U were $1.26 \cdot 10^{-6}$, $6.90 \cdot 10^{-7}$, $4.90 \cdot 10^{-8}$, $4.50 \cdot 10^{-8}$ Sv/Bq, respectively.

Results and discussion

In recent years, there has been growing awareness of the radiological content in marine foodstuffs due to the significant impact that their ingestion can have on the ingestion dose received by humans. As reported in the literature, molluscs have the ability to bio-accumulate radionuclides present in the water media in which they live (Stepnowski and Skwarzec 2000; Mishra et al. 2009; Raja and Shahul Hameed 2010; Feroz Khan et al. 2011; Rozmaric et al. 2012; Musthafa and Krishnamoorthy 2012; Kristan et al. 2015).

In the evaluated area, it is important to highlight that there are different industrial activities which can have an effect on the radiological quality of the water of the Ebro River. In this regard, there is NORM industry, concretely a dicalcium phosphate plant (DCP) up-stream of the area in which the samples were taken.

In particular, the activity concentrations were determined for natural radio-isotopes (^{210}Po, ^{210}Pb, ^{234}U, ^{238}U, ^{232}Th and ^{230}Th) from different bivalves (razor shells, large oysters, clams and mussels) typically produced and consumed in that area, and presented in Table 1 for sample dry weight. Another species, sea snail (murex brandaris), which is a gastropod, was considered as a reference sample in this study as it lives in the deep sea and does not therefore come into direct contact with water from Ebro River which flows into the bays where the analyzed bivalve organisms live. Despite some authors reported that this specie accumulate lower amount of radionuclides (Raja and Shahul Hameed 2010; Khan and Wesley 2012; Uddin and Bebhehani 2014), we have considered that in our study this specie can be a reference specie because is the unique specie cultivated outside the bays. The results obtained in the determination of the different radionuclides are shown in Table 1 in terms of dry weight (d.w.). Moreover, it is important to highlight that sampling was performed in two seasons (winter and summer), as other studies reported that isotope concentration can vary depending on different factors, such as seasonal changes (Connan et al. 2007; Carvalho et al. 2011; Strok and Smodiš 2011; Aközcan 2013; Uddin and Bebhehani 2014; Bode et al. 2015).

In the present study, ^{210}Po was found to be the main contributor to the radiological content of all of the analyzed samples in both the winter and summer seasons, with activity values ranging between 263.1 and 813.0 Bq/kg (d.w.). In general, as was demonstrated by different authors, ^{210}Po is taken up by plankton and assimilated in their cells at higher levels. Therefore, ^{210}Po is considerably accumulated at high concentrations in soft tissues, specifically proteins, and it can even be accumulated by marine vertebrates (Stepnowski and Skwarzec 2000; Carvalho 2011; Rozmaric et al. 2012; Kilic et al. 2014; Renaud et al. 2015).

Meanwhile, the values found for this isotope in the two evaluated seasons do not show significant differences for all of the molluscs, except in the case of mussels where great variability could be observed depending on the season (263.1 ± 26.6 Bq/kg in summer whereas, for winter, the obtained value was 813.0 ± 72.9 Bq/kg). As can be observed from these results, the activity values were considerably higher in the cold season in comparison to the warm one, as previously reported in the literature, and mentioned earlier (Carvalho et al. 2011; Strok and Smodiš 2011). However, in our case, the observed differences between the two seasons were even higher. This may probably be due in part to the body size of the analyzed mussels, which was higher in spring and this may contribute to the lower activity in the warm season. Previous studies have reported that this parameter can also have an influence on the measured activity, such as the study by Strok and Smodiš (Strok and Smodiš 2011).

Briefly, it can be concluded that the observed differences between gastropods and bivalves for ^{210}Po in our case may be attributed to both the sampling area and the type of molluscs. In the literature, higher activities of ^{210}Po have been found in bivalves from an area influenced by industrial activities. Examples include a study by Aközcan (Aközcan 2013) in which samples were collected in Turkey in areas where some NORM industries operated, such as iron and steel factories, fuel storage yards, fertilizer factories and a natural gas power plant, among others, all of which discharge raw solid and liquid waters into the sea. In this case, results for bivalves

Table 1. Activity concentration (Bq/kg d.w.) of the selected radioisotopes of different molluscs in the Ebro Delta area with given expanded uncertainties (k = 2).

Sample type	Season	Activity concentration dw (Bq/kg)				
		^{210}Po	^{210}Pb	^{234}U	^{238}U	^{210}Po/^{210}Pb
Razor shells *Ensis arcuatus*	Winter	427.1 ± 33.9	6.9 ± 0.7	7.5 ± 1.7	5.9 ± 1.4	61.6
	Summer	433.8 ± 52.7	9.6 ± 0.5	3.9 ± 0.9	2.9 ± 0.6	45.0
Large oyster *Crassostres gigas*	Winter	399.5 ± 29.4	4.1 ± 0.2	2.9 ± 0.7	2.4 ± 0.6	97.7
	Summer	356.1 ± 33.8	1.4 ± 0.3	3.3 ± 0.8	2.7 ± 0.7	256.5
Clam *Ruditapes philippindrum*	Winter	545.8 ± 51.4	1.4 ± 0.1	1.3 ± 0.3	1.1 ± 0.2	403.8
	Summer	506.8 ± 44.2	1.3 ± 0.2	2.0 ± 0.4	1.9 ± 0.4	398.3
Mussels *Mytilys edulis*	Winter	813.0 ± 72.9	3.4 ± 0.2	0.8 ± 0.2	0.9 ± 0.2	240.6
	Summer	263.1 ± 26.6	5.4 ± 0.2	1.0 ± 0.3	0.9 ± 0.2	48.4
Sea snail* ***Murex brandaris***	**Winter**	**69.6 ± 6.6**	**6.8 ± 0.2**	**3.2 ± 0.7**	**3.4 ± 0.7**	**10.2**
	Summer	**54.1 ± 6.2**	**4.1 ± 0.2**	**3.2 ± 1.0**	**2.0 ± 0.6**	**13.2**

*reference point

were in the range of 332 to 776 Bq/kg (d.w.) for ^{210}Po. In contrast, lower values of activity concentration were found in bivalves sampled in other areas not influenced by industrial activities or industrial discharges. The objective of these studies was to acquire baseline data on the concentration of natural radionuclides in certain common molluscs, and some examples include the study by Musthafa and Krishnamoorthy (Musthafa and Krishnamoorthy 2012) and Raja and Shahul Hameed (Raja and Shahul Hameed 2010). They made an estimation of ^{210}Po in marine organisms in Ennore Creek (southern India) and Parangipettai Coast (south-east coast of India), respectively. The activities of ^{210}Po found in bivalves (different species of mussels) ranged between 96.12 and 113.32 Bq/kg and between 91.6 and 132.4 Bq/kg, respectively. They conclude that bivalves accumulate the highest concentration for ^{210}Po, suggesting that they could serve as a bio-indicator of the presence of radionuclides.

In the case of ^{210}Pb, the values recorded are also summarized in Table 1 and they ranged between 1.3 ± 0.2 Bq/kg in the case of clams and 9.6 ± 0.5 Bq/kg for razor shells. In the literature, the values found in our study are in the same range as activities found in mussels from Portugal (Carvalho 2011), Croatia (Rozmaric et al. 2012) and India (Raja and Shahul Hameed 2010). Examples include the study by Khan and Godwin Wesley (Khan and Godwin Wesley 2011), which determined natural radionuclides in mussels from a non-industrial area on a tropical coast (India). The background levels found of ^{210}Pb in this area were 7.2 ± 0.1 Bq/kg. In contrast, in the study by Strok and Smodiš (Strok and Smodiš 2011), which focuses on an area influenced by industrial activity (a former uranium mine), the values found in bivalve samples (mussel and oysters) from the Slovenian part of the Adriatic Sea ranged between 1.1 and 3.0 Bq/kg.

The ^{210}Po/^{210}Pb activity ratio was also investigated (see Table 1). In this case, the ratio between ^{210}Po and ^{210}Pb varied between 45.0 and 403.8. As can be observed, the obtained values for ^{210}Pb are considerably lower than those obtained for ^{210}Po. This can be explainned by the higher affinity of ^{210}Po for organic matter, as was reported previously by several authors (Idoeta et al. 2011; Mohamed et al. 2013). These values are in higher ranges than in the study by Boisson *et al*. (Boisson et al. 2001), which found a ^{210}Po/^{210}Pb radio of 48 in the bivalve *Tellina tenuis* collected in a vent zone off the coast of Milos Island (Mediterranean sea). They are also higher than the study by Strok and Smodis (Strok and Smodiš 2011) and the study by Rozmaric et al. (Rozmaric et al. 2012) which found a ^{210}Po/^{210}Pb ratio of 16.9-113.3 and 6.2-30.7 in bivalve *Myllitus galloprovin-*

cialis, respectively on the Adriatic Coast. These ratios may also indicate that the ^{210}Po activity concentrations in the samples do not only occur from the ^{238}U decay chain, but other sources as well.

With respect to uranium and thorium isotopes (Table 1), based on the obtained results, it can be observed that, in all of the analyzed samples, a higher activity concentration of uranium isotopes was recorded than for thorium isotopes. This is because uranium is highly soluble in water, whereas thorium displays completely different behaviour. The activity concentration of uranium isotopes ranged between 0.8 and 7.5 Bq/kg, and 0.9 and 5.9 Bq/kg for ^{234}U and ^{238}U, respectively. As expected, concentration values of thorium isotopes were below the minimum detectable activity (MDA) of 0.5 Bq/kg (Khandaker et al. 2013). In the literature, there are a few studies that focus on measuring uranium and thorium isotopes in molluscs. For example Khandaker *et al.* (Khandaker et al. 2013) determined a group of natural radionuclides (^{238}U, ^{232}Th and ^{40}K) in shellfish from peninsular Malaysia. That area is exposed to radiation due to rapid industrialization over the last few decades, including phosphate-processing industries among others. The average concentration of ^{238}U in molluscs was 4.15 Bq/kg, whereas the average concentration values of ^{232}Th were the lowest of all of the included radionuclides (1.76 Bq/kg). The authors conclude that this result is partly explained by the different solubility of the two isotopes in water This may be the reason for the lower accumulation of thorium in the edible parts of seafood.

Briefly, based on all of the obtained results, it can be concluded that water from the Ebro River can transport radionuclides present in the area surrounding the dicalcium phosphate plant. This industrial activity can enhance the levels of naturally occurring radioactivity isotopes in the aquatic ecosystem which leads to bioaccumulation by organisms which are filter feeders.

Committed dose from annual intakes

The consumption of molluscs is a significant part of the Mediterranean diet. For this reason, it is important to estimate the radiation dose due to the consumption of seafood, especially in those cases where the waters were fish feed can be influenced by industrial activities such as the coal and phosphate processing industries.

The annual effective ingestion dose for all the measured isotopes in the analyzed species was calculated with the equation given in Section 2.5. As mentioned, this dose depends on several parameters, such as the radionuclide under consideration and the age of the individuals being analyzed. In this study, the annual committed effective dose was evaluated for each radionuclide in the adult age range (>17 years). The value corresponding to the estimation of the annual intake in each molluscs species was taken from AESSAN (Agencia Española de Seguridad Alimentaria y Nutrición; Ministerio de Sanidad; Servicios Sociales e Igualdad) (2011) and are given in Table 2. Moreover, it should be considered that, in order to perform the calculation of the dose, the activity concentration should be expressed in terms of wet weight, and, in order to do so, an estimation was used of the ratio between wet weight and dry weight.

The effective doses resulting from the intake of ^{238}U, ^{234}U, ^{210}Pb and ^{210}Po from the consumption of all of the species under consideration in this study are reported in Table 2. The obtained values ranged between 1.48 µSv/y and 148.91 µSv/y, and it can be concluded that the total annual effective ingestion dose due to the consumption of all of these species for the adult population in the area under study was estimated at 236.01 µSv/y. The ingestion doses calculated for all of the molluscs sampled were in the typical range of total ingestion exposure due to natural radiation published by UNSCEAR (UNSCEAR 2008), which is 200-1,000 µSv/y.

The values found in our study are comparable with other studies reported in the literature, which focus on other regions around the world. However, it is important to highlight that the average consumption of molluscs in each country should also be taken into consideration for comparison purposes. For example, in their study, Musthafa and Krishnamoorthy (Musthafa and Krishnamoorthy 2012) establish baseline data on the radiation profile via the consumption of *Mytilus galloprovincialis* in Ennore Creek (southern India), which was 183.92 µSv/y. In contrast, it is also interesting to highlight the study by Strok and Smodiš (Strok and Smodiš 2011), which focuses on Slovenia, a country with low consumption of molluscs in the diet. The annual effective ingestion dose which they reported due to ^{210}Po from mussel consumption was 8.5 µSv/y. This means that, depending on the place and the amount of molluscs consumed in their diet, the annual effective ingestion dose can vary considerably.

Conclusions

The levels of naturally occurring radionuclides from the ^{238}U and ^{232}Th series were determined in different molluscs typically produced and consumed in the Ebro Delta area. The results showed an activity concentration of ^{210}Po between 263.1 ± 26.6

Table 2. Annual effective ingestion dose through the intake of molluscs.

Sample type	**Yearly consumption (kg/person/year)**	**Annual effective ingestion dose due to the individual radionuclide (µSv/year)**			
		^{210}Po	**^{210}Pb**	**^{234}U**	**^{238}U**
Razor shells *Ensis arcuatus*	0.04	4.81	0.07	0.04	0.03
Large oyster *Crassostres gigas*	0.01	1.48	0.01	0.01	0.01
Clam *Ruditapes philippindrum*	0.64	76.13	0.10	0.01	0.01
Mussels *Mytilus galloprovincialis*	1.15	148.91	0.68	0.01	0.01
Sea snail* ***Murex brandaris***	**0.17**	**3.51**	**0.17**	**0.01**	**0.01**

*reference point

and 813.0 ± 72.9 Bq/kg (d.w.), which was higher than the usual activities found in areas not affected by industrial activity. These high values can probably be attributed to the impact of the industries, which increase the amount of naturally occurring radio-nuclides in the Ebro River basin, such as the dicalcium phosphate plant located a few kilometres upstream from the Ebro Delta.

Committed effective ingestion doses were calculated for all of the molluscs. The total amount from all of the species was 236.01 µSv/y, which is within the typical range published by UNCEAR (UNSCEAR 2008) in terms of total ingestion exposure.

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3.1.3. Discussió de resultats

En aquest estudi, s'han quantificat els diferents radionúclids d'origen natural (^{210}Po, ^{210}Pb, ^{234}U, ^{238}U, ^{232}Th i ^{230}Th) en diferents bivalves (navalles, ostres, cloïsses i musclos). A més, s'ha analitzat també el cargol de mar com a espècie de referència, donat que aquesta espècie viu fora de la badia, i no està en contacte amb les aigües i sediments del riu. El mostreig es va dur a terme en dues estacions meteorològiques diferents, per tal d'avaluar el possible impacte dels canvis estacionals.

Els resultats obtinguts en les dues estacions avaluades no mostren diferències significatives pels diferents mol·luscs, a excepció del ^{210}Po en els musclos. En aquest cas, s'ha vist força desigualtat (263.1 ± 26.6 Bq/kg a l'estiu mentre que a l'hivern va ser de 813.0 ± 72.9 Bq/kg). Com es pot veure a través dels resultats, a l'hivern els valors són considerablement més elevats en comparació amb els de l'estiu, i aquesta tendència coincideix amb alguns estudis de la bibliografia [1,2]. Tot i així, no s'han pogut atribuir aquestes diferències d'activitat només a l'estació meteorològica, perquè hi ha diferents factors que també poden afectar, tals com la mida dels musclos analitzats i el cicle biològic en el que es troben [3].

Globalment, el ^{210}Po és el principal contribuent del contingut radiològic en els mol·luscs analitzats en totes dues estacions. Comparant totes les espècies analitzades, cal destacar que els cargols de mar (espècie de referència) presenten les concentracions de ^{210}Po més baixes (54.1 – 69.6 Bq/kg). Tenint en compte l'estudi de Uddin i col. [3] on s'ha determinat el contingut de ^{210}Po en dos espècies de gastròpodes *Stomatella aurícula* i *Cerithium scabridum* (10.4 – 12.4 Bq/kg i 52.6 – 60.5 Bq/Kg pes sec, respectivament), no podem assegurar que el baix contingut sigui degut al tipus de mol·lusc, ja que el règim d'alimentació que té cadascuna de les espècies també pot influir.

En diversos estudis de la bibliografia en què es determina ^{210}Po en bivalves, s'ha pogut veure una certa influència de les indústries NORM en la concentració d'activitat obtinguda. Per exemple, Aközcan [4] en el seu estudi, determina l'activitat de musclos d'un àrea on operen diferents indústries NORM (indústries extractores de metalls, plantes de fertilitzants, etc.). Les activitats de ^{210}Po obtingudes han estat entre 332 i 776 Bq/kg. En canvi, s'han obtingut concentracions més baixes en àrees no influenciades per activitats industrials o abocaments industrials (al voltant de 90 i 130 Bq/kg) [5,6].

Pel que fa al ^{210}Pb, les activitats són força més baixes que en el cas del ^{210}Po. S'ha obtingut una relació ^{210}Po/^{210}Pb entre 45.0 i 403.8. Aquest fet pot ser explicat per l'afinitat del ^{210}Po a la matèria orgànica, com s'ha vist en diferents estudis [7,8]. A més aquesta relació indica que l'activitat de ^{210}Po obtinguda en les mostres no només prové de la cadena de decaïment de l'^{238}U.

En el cas dels isòtops d'urani i tori, en els resultats es pot veure que en totes les mostres analitzades s'han obtingut valors d'urani més elevats que de tori. Un motiu pot ser perquè l'urani és molt més soluble en aigua, mentre que el tori té un comportament diferent. Les activitats dels isòtops d'urani varien entre 0.8 i 7.5 Bq/kg, i 0.9 i 5.9 Bq/kg per a l'^{234}U i ^{238}U, respectivament. En canvi, com era d'esperar totes les activitats dels isòtops de tori estaven per sota de l'activitat mínima detectable (0.3 Bq/L).

Finalment, amb les activitats obtingudes es va fer una estimació de les dosis per ingesta d'aquests mol·luscs. Els resultats individuals obtinguts pels diferents radionúclids van ser entre 1.48 i 148.91 µSv/any, i la dosi total per ingesta de mol·luscs pel que fa als radionúclids analitzats va ser de 236 µSv/any. Aquestes dosis obtingudes estan dintre de l'interval d'ingestió total degut a la radiació natural publicada per la "*United Nations Scientific Committee on the Effects of Atomic Radiation* (UNSCEAR)" [9], que és 200 – 1000 µSv/any. Per acabar cal destacar que aquestes dosis no poden ser realment comparades amb les obtingudes en altres països ja que depenen del consum mitjà d'aquestes espècies a cada país.

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Capítol 4

CONCLUSIONS

En aquest últim capítol de la tesi, exposarem les principals conclusions obtingudes en els diferents estudis d'investigació, dedicats principalment a la determinació de radionúclids tant naturals com artificials procedents de la industrialització al tram baix del riu Ebre.

1. S'ha optimitzat i validat un mètode per a la separació i posterior determinació de ^{55}Fe i ^{63}Ni en mostres de fangs procedents d'una planta de tractament d'aigua potable (ETAP).

2. En l'avaluació de l'activitat de ^{55}Fe i ^{63}Ni en les mostres de fangs de l'ETAP estudiades s'han observat activitats considerables en alguns mesos, fins a nivells de 162 i 65 Bq/kg per al ^{55}Fe i ^{63}Ni, respectivament.

3. S'ha verificat que la problemàtica en la quantificació del ^{55}Fe en la matriu de fangs de l'ETAP, és deguda a una reacció de quimioluminescència provocada per l'alt contingut de Fe (III) en la matriu.

4. Mitjançant diferents proves, s'ha pogut accelerar la reacció de quimioluminescència (deixant les mostres durant 8 hores de 40 ºC a 60 ºC). Tot i així, a elevades temperatures no s'ha garantit l'estabilitat del líquid d'escintil·lació, per tant, cal destacar que la millor opció ha estat deixar les mostres a temperatura ambient durant una setmana abans de mesurar-les.

5. S'ha optimitzat i validat un mètode per a la separació de ^{210}Po en mostres d'aigües, fangs procedents de l'ETAP i mostres de biota (peixos, cargols i musclos).

6. Tot i que les activitats de ^{210}Po obtingudes en els fangs no han estat gaire elevades (31 - 42 Bq/kg), ja que estan en el mateix interval de magnitud que les d'un sòl estàndard, s'han pogut veure activitats superiors en algunes de les mostres de biota analitzades. Per exemple, les concentracions d'activitat de ^{210}Po obtingudes en el cargol poma i els musclos han estat entre 164 ± 37 Bq/kg i 366 ± 10 Bq/kg, això suggereix que pot haver una influència de la indústria de fosfat bicàlcic situada aigües amunt de la desembocadura del riu on s'han mostrejat aquestes espècies.

7. Sabent la relació entre l'aigua d'entrada a l'ETAP i els fangs generats, s'ha pogut fer una estimació de la concentració de ^{55}Fe, ^{63}Ni i ^{210}Po en l'aigua d'entrada a la planta mitjançant la concentració d'activitat obtinguda d'aquests radionúclids en els fangs. Amb aquesta estimació, s'evitaria desenvolupar un mètode per determinar

l'activitat d'aquests radionúclids en les mostres d'aigua d'entrada (que requereix gran volums de mostra).

8. En l'estudi de l'avaluació de la concentració de radionúclids naturals en els mol·luscs que es cultiven al delta de l'Ebre, les activitats obtingudes dels radionúclids naturals, majoritàriament de ^{210}Po, han estat més elevades que les que es troben normalment en zones no afectades industrialment (263.1 ± 26.6 – 813.0 ± 72.9 Bq/kg). Tot i obtenir activitats força elevades, no s'han pogut atribuir totalment a la presència de les indústries que hi ha al llarg del riu Ebre, ja que poden influir altres factors tals com la geologia del terreny.

9. Finalment, per tal d'estimar la dosi a través de la ingesta, s'ha considerat que l'activitat de cadascun dels radionúclids es absorbida l'organisme. Els valors dosi calculats mostren que, en general, no existeix cap risc per a la salut de la població que consumeix aquestes espècies en la seva dieta habitual, ja que està dintre de l'interval recomanat d'ingesta d'aliments amb aportació de radionúclids naturals publicada per la UNSCEAR.

Annexos

Radon in spring waters in the south of Catalonia

RADON IN SPRING WATERS IN THE SOUTH OF CATALONIA

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Abstract

Spring waters in the south of Catalonia were analysed to determine the ^{222}Rn activity in order to be able to establish a correlation between the obtained values with the geology of the area of origin of these samples, and also estimate the potential health risks associated with ^{222}Rn. Most of the analysed samples (90%) show ^{222}Rn activities lower than 100Bq/L (exposure limit in water recommended by the World Health Organisation and EU directive 2013/51/EURATOM). However, in some cases, the activity values found for this isotope exceeded those levels and this can be attributed to the geology of the area where the spring waters are located, which is predominantly of granitic characteristics. To verify the origin of the radon present in the analysed samples, the obtained activity values were compared with the activities of its parents (^{226}Ra, ^{238}U and ^{234}U). Finally, we have calculated the annual effective dose from all the radionuclides measured in spring water samples. The results showed that the higher contribution due to spring water ingestion come from ^{222}Rn and ^{226}Ra. The resulting contribution to the annual effective dose due to radon ingestion varies between 10.2 and 765.8 µSv/y, and the total annual effective dose due to his parents, ^{226}Ra, ^{234}U and ^{238}U varies between 0.8 and 21.2 µSv/y so the consumption of these waters does not involve any risks to population due to its natural radioactivity content.

Keywords: *spring water, uranium, radium, radon, LSC, annual effective doses.*

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1. Introduction

Drinking water is usually provided by groundwater or surface water sources. Different substances present in the water source, such as radioactive elements, can dissolve in water and contaminate drinking water resources. The content of these natural radionuclides in groundwater can vary in several orders of magnitude and are influenced by physical (temperature), chemical (pH) and geological properties of the aquifer (Duggal et al., 2013; Isam Salih et al., 2002; Jobbágy et al., 2010; Przylibski and Gorecka, 2014). For instance, felsic rocks, such as granite, present high contents of incompatible elements such as ^{40}K, ^{238}U and ^{232}Th (Moreno et al., 2014). Radium can occur in rocks, soils and sediments, so it can be found in virtually every aquifer matrix (Sahin et al., 2013; Todorovic et al., 2012).

Radon (^{222}Rn), a decay product of ^{226}Ra, is a naturally occurring inert radioactive gas with a half-life of 3.82 days. When ^{226}Ra decays, ^{222}Rn atoms might be ejected from the soil grain by α-recoil and transferred to groundwater or void air and finally escape through the atmosphere (Abdallah et al., 2007; Somlai et al., 2007; Tabar and Yakut, 2014).

The primary health effect of ^{222}Rn is lung cancer, resulting from inhalation in indoor air. There is also evidence from epidemiology that ingestion of ^{222}Rn causes stomach cancer (Ravikumar and Somashekar, 2014; Todorovic et al., 2012).

In order to protect the population from radiation exposure from ^{222}Rn it is necessary to analyse the presence of this radionuclide on the water sources, particularly underground sources. In this respect, an European Directive has been published recently laying down the requirements for the protection of the health of the general public with regard to radioactive substances in water intended for human consumption (EURATOM, 2013). The recommended reference level of effective dose received from drinking water consumption is 100 µSv/y. This value excludes the dose received from ^{3}H, ^{40}K, ^{222}Rn and its decay products but a specific reference value of 100 Bq/L for ^{222}Rn has been also established. However, it should be pointed out that these recommendations do not apply to natural mineral waters and waters that are classified for medical benefits.

This study focuses on the determination of ^{222}Rn at different points in northeastern Spain, in the region of Catalonia, where numerous lithologies outcrop. The presence of numerous natural springs points to the possibility of elevated radioactivity and ^{222}Rn activity depending on the mineral composition of the rocks. In this respect, one important objective is to correlate the possible origin of this isotope through the analysis of its parents (^{226}Ra, ^{234}U and ^{238}U). Another aim is to determine the health hazards from the consumption of this water through the evaluation of the annual effective radiation dose.

2. Materials and methods

2.1 Materials and reagents

All chemical reagents used in this study were of analytical grade. Hydrochloric acid (37%), nitric acid (65%), hydrogen peroxide (30%), ammonia solution (25%), iron chloride (III), citric acid anhydrous and sulphuric acid were supplied by J.T. Baker (Deventer, Holland). Barium chloride dehydrate, lead nitrate, calcium nitrate tetrahydrate and sodium sulphate were supplied by Sigma-Aldrich. UTEVA columns were supplied by Eichrom (Bruz, France). A mineral oil scintillator (Ultima Gold F) and Optiphase Hisafe^{TM} 3 were provided by Perkin Elmer^{TM} (Turku, Finland).

A solution of ^{241}Am with a nominal activity concentration of 4.68±0.41 KBq/g was provided by Amersham International, PLC (Buckinghamshire, England). Standards of ^{232}U and ^{226}Ra certified solutions with a well-known activity concentration value of 15.01 ± 0.15 Bq/g and 175.9 ± 0.7 Bq/g were provided by CIEMAT (Centro de Investigaciones Energéticas, Medio-ambientales y Tecnológicas - Madrid, Spain).

Uranium was electroplated onto stainless steel planchets (diameter 25.15 mm and thickness 0.6 mm) supplied by Tecnasa (Madrid, Spain). Samples were filtered with a 0.45 µm filter supplied by Whatman (Maidstone, United Kingdom).

For the measurement of ^{222}Rn, Teflon-coated polyethylene vials with a volume of 20 mL were used, equipped with urea screw caps and aluminium foil liners. They were supplied by Perkin Elmer^{TM}.

2.2 Detectors

^{226}Ra was measured using a zinc sulphide (ZnS [Ag]) scintillator counter (photo multiplier tube and base preamplifier) model 2000 Canberra (Meriden, Connecticut) with a voltage range of 0.76 to 0.90 KeV. A planchet containing ^{241}Am with an activity concentration of 100 Bq was used for the monthly calibration. The background of each detector was determined by counting an empty planchet for 5,000 minutes.

An alpha spectrometer was used to determine the individual isotopes of uranium (^{238}U, ^{235}U and ^{234}U). The alpha spectrometer (EG&G ORTEC, Model 676A, Oak Ridge, Tennessee) includes an ion-implanted silicon detector (ORTEC, size: 450mm^2; alpha resolution: 25keV FWHM at 5.48 MeV of ^{241}Am) in a vacuum chamber (Edwards Model E2M8, Sanborn, New York), a detector bias supplier, a preamplifier, a linear amplifier, and a multichannel pulse height analyser. Throughout the measurement, the pressure of the chamber was maintained at 1.06kPa (10^{-2}Torr).

^{222}Rn was determined by ultra-low level liquid scintillating counting (LSC) in a Quantulus 1220^{TM} from Perkin-Elmer (Turku, Finland) with WinQ and Easy View software.

2.3 Methods

The method used to determine the uranium isotopes (^{234}U, ^{235}U and ^{238}U) was described in a previous study by Mola *et al.* (Mola et al., 2013). In brief, this method consists of the precipitation of the actinides and separation of the uranium using an UTEVA resin (Eichrom, Bruz, France). The uranium solution was then transferred to an electrodeposition cell and the uranium isotopes were electrodeposited for 2 hours, under a current density of 1.5 A/cm^2. One minute before the end of the electrolysis, 1mL of concentrated ammonium hydroxide was added to ensure uranium deposit attachment on the stainless steel disk.

To determine ^{226}Ra, a method described by Palomo *et al*. (Palomo et al., 2007) was followed. This method is based on co-precipitation using barium chloride and sulphuric acid. Different clean-up steps were then applied to adjust the solution to different pH levels. Finally, the barium sulphate /radium sulphate precipitate was formed and isolated. This precipitate was deposited on a planchet for measurement in the ZnS (Ag) counter.

In the case of ^{222}Rn, the determination method consisted of taking an aliquot of 10 mL of sample (sampling details explained in Section 2.4) which was placed in a Teflon-coated polyethylene vial. This was then mixed with the scintillation cocktail Ultima Gold F until there was no empty space in the vial (about 12 mL). The vial was stirred vigorously and left in the instrument for 4h prior to the measurement to attain equilibrium between ^{222}Rn and its progeny. The window for ^{222}Rn was set between 650 and 910 channels to be able to determine ^{222}Rn and its daughters ^{214}Po and ^{218}Po (Aleissa et al., 2013; Jowzaee, 2013; Salonen, 2010). Counting was performed for two cycles of 500 minutes. Pulse shape analysis (PSA) measurement mode was used for ^{222}Rn and in order to separate alpha and beta pulses into different spectra electronically.

2.4 Water samples

Sample locations of the analysed natural spring waters (15 samples) were considered on the basis of the different lithologies encountered (Table 1). Natural spring water samples were collected directly in 2L nalgene plastic containers for the determination of different radioactive isotopes. In addition, for the determination of ^{222}Rn, 100 mL of each sample were also collected in a glass bottle to avoid gas bubble formation. The samples were then capped immediately to prevent ^{222}Rn to degas into the atmosphere.

2.5 Ingestion doses

The annual effective radiation dose (E_D) for an individual consumer due to the water intake is calculated using the equation:

$$E_D = Ac \cdot Ia \cdot C_f$$

where Ac is the activity concentration from each radionuclide of ingested water in terms of Bq/L, I_a describes the annual intake of drinking water (the WHO and EPA estimate the average consumption of water in 2 L of water per day, 730 L/y) and C_f is the coefficient dose for adults, with a value of $6.5 \cdot 10^{-8}$, $2.8 \cdot 10^{-7}$, $4.9 \cdot 10^{-8}$, $4.5 \cdot 10^{-8}$ and $1 \cdot 10^{-8}$ Sv/Bq, for ^{224}Ra ^{226}Ra ^{234}U ^{238}U and ^{222}Rn, respectively (UNSCEAR, 2008).

3. Results and discussion

3.1 Optimization of LSC method for ^{222}Rn determination

Firstly, we evaluated the effect of several parameters on the counting efficiency by LSC. In particular, we focused on the selection of the liquid scintillation cocktail and the sample volume needed to achieve the highest efficiency possible. For the optimization, a ^{226}Ra standard was used and, prior to the measurement, Teflon-coated vials was sealed to avoid ^{222}Rn degassing. An equilibration time of 21 days was needed to ensure decay equilibrium between ^{226}Ra and its progeny (^{222}Rn). For background measurement, an additional vial was prepared containing a mixture of cocktail and deionized water.

Two of the most common cocktails previously in the literature for the determination of ^{222}Rn were compared: Ultima Gold F (Salonen, 2010; Schubert et al., 2014) and Optiphase Hisafe ^{TM} 3 (Maragheh et al., 2002; Stojkovic et al., 2015). To do so, the first series of liquid scintillation samples were prepared with Teflon-coated polyethylene vials. The vials were completely filled with approximately 12 mL of the scintillation cocktail and with a fixed ^{226}Ra standard volume of 10 mL. From the results obtained, no significant difference could be observed between the efficiency of the two cocktails used. The best results were obtained with the Ultima Gold F cocktail, with an efficiency of 300%. This is higher than 100% because the sum of the counts of all of the ^{226}Ra progeny present in the spectrum (^{222}Rn, ^{218}Po and ^{214}Po) are used for efficiency calculation. In addition, this cocktail allows distingui-

Table 1. Name, location, geology and chemical parameters measured in situ of the different natural spring waters.

Sample number	Geology (rocks types)	Location		Conductivity* µS	Turbidity* (NTU)	Temperature* ºC	pH*
		Latitude	Longitude				
1●	Beige limestones and marlstones. On a fault.	40º39'20.21''N	0º16'6.05''E	530	0.3	15	7.1
2●	Limestones with marlstones levels.	40º39'46.07''N	0º15'54.04''E	610	0.3	16.4	7.3
3●	Limestones with marlstones levels.	40º40'4.9''N	0º28'38.3''E	593	0.8	17.9	7.3
4●	Dolomite, limestones, sandstones and clays.	40º54'32.8''N	0º22'59.3''E	473	0.1	13.5	7.9
5●	Limestones and dolomite interbedded with marl.	40º50'43.3''N	0º21'11.6''E	474	0.1	12.9	8.4
6●	Limestones biomicritics.	41º8'3.3''N	1º16'17.3''E	3953	0.3	18.1	7.9
7▪	Conglomerates with clay matrix.	41º20'50.4''N	1º21'44.5''E	957	0.3	16.7	7.5
8◊	Alkaline granites and granodiorites. On a fault.	41º19'40.0''N	0º59'26.5''E	220	0.3	11.3	7.6
9◊	Alkaline granites and granodiorites. On a fault.	41º18'36.6''N	0º59'22.8''E	420	0.6	14.4	7.1
10◊	Alkaline granites and granodiorites.	41º18'34.1''N	0º59'19.9''E	745	17.4	13.8	7.3
11†	Siliceous sandstones and clays.	41º18'28.0''N	0º59'14.1''E	255	0.2	11.4	8.8
12†	Siliceous sandstones and clays.	41º18'32.1''N	0º59'23.4''E	584	0.8	13.2	7.9
13†	Siliceous sandstones and clays.	41º18'31.2''N	0º59'11.2'' E	254	0.7	12.1	8.3
14●	Limestones with marlstones levels.	40º0'5.4''N	0º0'7.0''E	442	0.6	16.5	7.7
15●	Limestones with marlstones levels.	40º21'59.0''N	0º08'13,1''E	486	0.1	16.7	7.7

* In situ measurements

●	Limestones, marlstones, sandstones, dolomite.
▪	Conglomerates with clay matrix.
◊	Alkaline granites and granodiorites.
†	Siliceous sandstones and clays.

-shing the different isotopes that are present in the obtained spectrum, so the peaks of ^{226}Ra progeny are more clearly separated than in the spectrum obtained for the other cocktail tested (Optiphase Hisafe^{TM} 3). Figure 1 shows the spectraof both scintillation cocktails, Ultima Gold F and Optiphase Hisafe^{TM} 3.

The next step was the optimization of the ratio between the sample and the scintillation volumes to achieve the maximum counting efficiency. In this case, a series of samples were used containing different volumes of ^{226}Ra standard in deionized water in the range of 8 to 16 mL and they were mixed with the scintillation cocktail until there was no empty space in the vial. The results showed that the counting efficiency obtained generally decreased as the sample volume increased and that the best results were obtained with a sample volume of 10 mL with an efficiency of 300%. This value is in line with the results previously reported in the literature by other authors applying similar conditions in terms of activity measurement (Kozlowska et al., 2010; Salonen, 2010; Schubert et al., 2014), as well as other authors using different cocktails, such as a mineral oil scintillator (Jowzaee, 2013; Landstetter and Katzlberger, 2009).

3.2 Validation of LSC method for ^{222}Rn determination

Trueness measured as relative bias

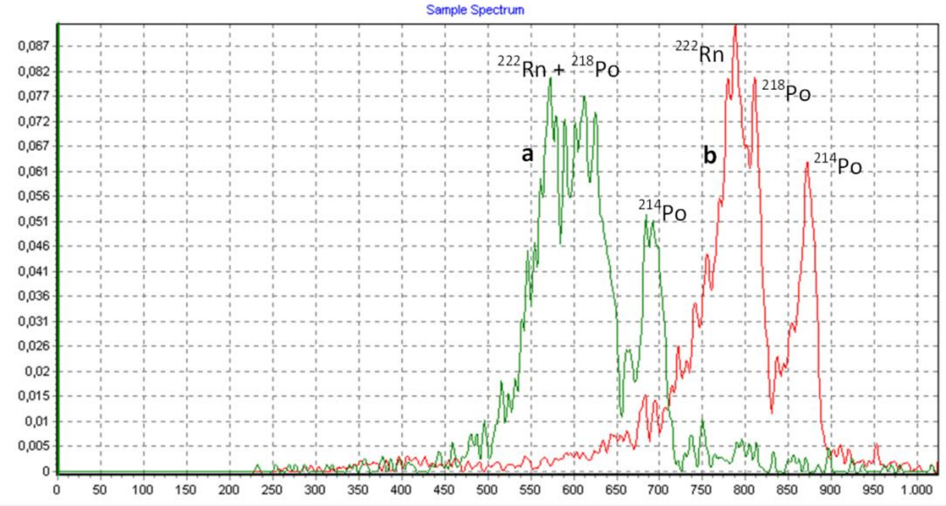

Fig 1. Alpha spectra of ^{226}Ra standard sample measured with Optiphase Hisafe 3 (a) and measured with the Ultima Gold F (b).

(RB), and precision as relative standard deviation (RSD), were evaluated for the optimized method for ^{222}Rn determination using spring water spiked with a known activity of ^{226}Ra in equilibrium with ^{222}Rn. Three replicas of the analysis of the validation sample were performed so the trueness and precision obtained were 4% and 11%, respectively. These values are low and similar to those reported in the literature (Salonen, 2010) for LSC measurements of ^{222}Rn. The minimum detectable activity (MDA) was 0.5 Bq/L and is also comparable to the values obtained by other authors (0.18-0.54 Bq/L) (Jowzaee, 2013; Kozlowska et al., 1999; Landstetter and Katzlberger, 2009). In this respect, the value of AMD obtained complies with the minimum limit of detection (10 Bq/L) established for ^{222}Rn measurement by the 2013/51/EURATOM Directive. Uncertainty was calculated by taking into account all of the uncertainty contributions and it ranged between 10.1% and 11.9% (K=2).

To verify the applicability of the method, a spring water sample was analysed that had previously been analysed by the LARUC Laboratory of the University of Cantabria, which is a national and international reference laboratory for ^{222}Rn measurements. This laboratory reported an activity of 171 ± 13 Bq/L of ^{222}Rn and the value found in our laboratory for this sample was 177 ± 13 Bq/L. Therefore, the results were comparable with a relative bias of 3.5 %. Based on all of these results, it was confirmed that the developed method provides satisfactory results.

3.3 Radioactivity characterization of natural spring water

The natural spring waters selected for this study were located on two contrasted lithologies: igneous rocks (granite: samples 8, 9 and 10) and soils of marine origin, such as limestones, marls and clays and carbonate formations (all other samples). The location, geology and chemical parameters measured in situ for these spring water samples are shown in Table 1. Figure 2 show the geological map of the studied region indicating the location of sampling points. The chemical/physical parameters measured in situ were the conductivity, turbidity, temperature and pH, as a number of previous studies reported in the literature have demonstrated a relationship between some of these parameters and ^{226}Ra activity. For example, Mehdizadeh et *al.* (Mehdizadeh et al., 2013) and Vidic et *al*. (Vidic et al., 2013) found waters from karstic and sedimentary terrains that ^{226}Ra activity values decreased at higher pH values. In a study by Aleissa *et al.* (Aleissa et al., 2013) a correlation between turbidity and the ^{222}Rn concentration in ground water was observed. It sums up that ^{222}Rn

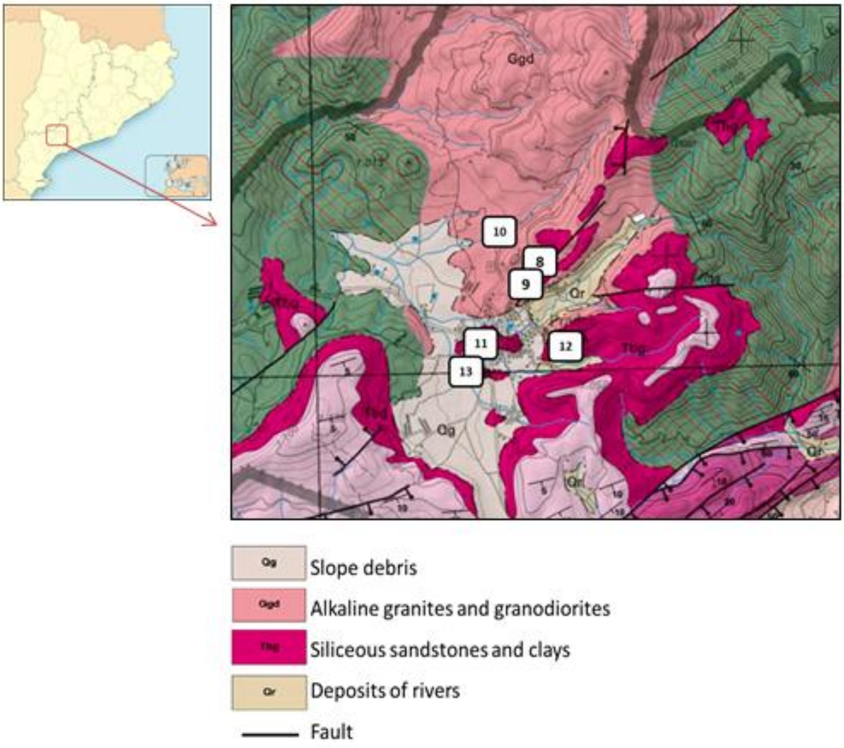

Fig. 2. Geological map of the Baix Camp region (Catalonia, Spain) showing the sampling points for some of the spring water samples analysed in this study.

concentration increases at higher levels of turbidity were negligible and based on the results obtained from the measurement of all those parameters; it was not possible to establish any correlation with the ^{222}Rn activities recorded. With respect to ^{222}Rn activities the measured values ranged from 1.4 to 104.9 Bq/L (Table 2). From these results, it should be highlighted that, for most of the analysed samples, the activity of ^{222}Rn was lower than the recommended value of 100 Bq/L established by WHO and EURATOM directives. However, in one case (sample 8), the obtained value is slightly higher than this recommended level (104.9 Bq/L). It should be noted that in this case the spring is located in a granitic terrain and close to an important fault. These geological features may explain this higher ^{222}Rn activity in comparison with the rest of the analysed samples. Fractures related to tectonic faults can create a higher emanation surface where ^{222}Rn can escape from the rock by α-recoil (Erdogan et al., 2013; Khattak et al., 2014; Popit and Vaupotič, 2002). In addition, granitic rock aquifers show

Table 2. Activity concentrations of naturally occurring alpha-emitting isotopes.

Sample number	Radon	^{226}Ra	Uranium (mBq/L)		
	(Bq/L)	(mBq/L)	^{234}U	^{238}U	^{234}U/ ^{238}U
1●	21 ± 1	6.0 ± 0.4	24 ± 2	12 ± 1	2.0
2●	9.9 ± 0.7	9.0 ± 0.4	22 ± 2	11 ± 1	2.0
3●	11.1 ± 0.8	3.0 ± 0.3	4 ± 0.7	4.4 ± 0.7	0.9
4●	4.1 ± 0.3	2.0 ± 0.3	10.2 ± 0.9	4.9 ± 0.6	2.1
5●	3.7 ± 0.3	2.0 ± 0.2	9 ± 1	4.9 ± 0.6	1.9
6●	7.5 ± 0.4	91 ± 1	55 ± 3	20 ± 2	2.8
7▪	3.4 ± 0.2	10.0 ± 0.5	31 ± 2	19 ± 2	1.6
8◊	105 ± 5	19.0 ± 0.6	29 ± 2	22 ± 2	1.3
9◊	89 ± 4	6.0 ± 0.4	19 ± 1	21 ± 1	0.9
10◊	32 ± 1	16.0 ± 0.6	23 ± 2	18 ± 2	1.3
11†	3.7 ± 0.2	7.0 ± 0.4	7 ± 1	8 ± 1	0.9
12†	7.0 ± 0.3	14.0 ± 0.6	22 ± 1	15 ± 1	1.5
13†	1.4 ± 0.1	3.0 ± 0.3	4 ± 1	4 ± 1	1.0
14●	3.1 ± 0.2	3.0 ± 0.3	5 ± 1	< 0.2	-
15●	2.7 ± 0.2	4.0 ± 0.3	13 ± 1	7 ± 1	1.9

●	Limestones, marlstones, sandstones, dolomite.
▪	Conglomerates with clay matrix.
◊	Alkaline granites and granodiorites.
†	Siliceous sandstones and clays.

higher ^{222}Rn concentrations than sedimentary rock aquifers because incompatible elements such as U concentrate in felsic rocks during magma differentiation (Abdallah et al., 2007; Jobbágy et al., 2010; Moreno et al., 2014; Pinti et al., 2014; Tabar and Yakut, 2014). It It should be noted that, in our study, samples originating from a granitic rock formation (8, 9 and 10) are the ones showing the higher activity values for ^{222}Rn in comparison with the samples obtained from the other geological areas. The other sampled points are relatively similar to each other with the exception of sample 1, which shows a slightly higher ^{222}Rn activity.

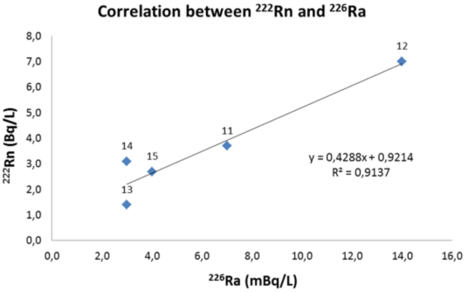

Fig.3. Correlation of ^{222}Rn and ^{226}Ra activity from the limestone and sandstone lithology (samples 11, 12, 13, 14 and 15).

In Table 3 we can see a summary of the information gathered by other researchers in different parts of the world. However, we cannot find a direct relation between lithology and ^{222}Rn because there are numerous factors which influence the mobility of the different nuclides in water.

In order to verify whether the activities of ^{222}Rn in the spring waters are related to the content of its parents (^{226}Ra, ^{234}U and ^{238}U) in the water or in the aquifer rocks, the activities of these radio-nuclides were determined and the results are shown in Table 2. Granitic samples showed higher contents of ^{222}Rn and ^{226}Ra, ^{234}U and ^{238}U, as can be seen in the case of Sample 8 (104.9 Bq/L of ^{222}Rn), with activities of 19.0, 29.1 and 21.6 mBq/L for ^{226}Ra, ^{234}U and ^{238}U, respectively. These activities are not correlated with the higher activities obtained for ^{222}Rn. This behaviour can be explained among other factors due to the higher solubility of this isotope in

Table 3. A comparison between ^{222}Rn concentrations in the groundwater and geology of the location.

Region	Rock type	^{222}Rn (Bq/L)	References
Garrotxa. Catalonia (Spain)	Volcanic region	0.8-26	(Moreno et al., 2014)
Riyadh (Saudi Arabia)	Limestone Sandstone	0.87-4.82 0.34-6.49	(Aleissa et al., 2013)
Southern part of Punjab State (India)	Kankar, sandy clay and sand	0.9-5.1	(Duggal et al., 2013)
Klodzka valley in the Sudety mountains (Poland)	Metamorphic rocks cut by many dislocation	0.18-89.3	(Kozlowska et al., 1999)
Transylvania (Romania)	Volcanic, mesozoic and flysch zone	2-129.3	(Cosma et al., 2008)
Yalova (Turkey)	Clay stone, sandstone, siltstone, conglomerate and marl	0.21-5.82	(Tabar and Yakut, 2014)
Southern Kohat Plateau (Pakistan)	Sandstones, shales and conglomerates	1.1-25.1	(Khattak et al., 2014)
Catalonia (Spain)	Granites Limestones Sandstones and clays	32.0-104.9 2.7-21.2 1.4- 7.0	Present study

water in comparison to isotopes of uranium and radium. Meanwhile, springs in areas of limestone and some other types of rocks, such as marlstones, sandstones and dolomite, displayed lower activities of ^{222}Rn (between 2.7 and 21.2 Bq/L), with activities of between 2.0 and 9.0 mBq/L, between 4.0 and 24.3 mBq/L and between <0.2 and 12.1 mBq/L for ^{226}Ra, ^{234}U and ^{238}U, respectively. This type of sample, in general, showed a correlation, but with another order of magnitude between ^{222}Rn activities and ^{226}Ra, as can be observed for Samples 11, 12, 13, 14 and 15 (Figure 3). Sample 6 presented a high content of ^{226}Ra and uranium isotopes, with values of 91 mBq/L, 55 mBq/L and 20 mBq/L for ^{226}Ra, ^{234}U and ^{238}U, respectively, although ^{222}Rn was also in disequilibrium at an activity of 7.5 Bq/L. It is important to take into account that Sample 6 also presented high conductivity (3,953 µS) and, since some authors have reported that there is a relationship between conductivity and radionuclide content in waters (Pujol and Sánchez-Cabeza, 2000), this could be the reason for the higher amount of radium and uranium present in this sample.

Additionally, the decay of ^{222}Rn in these samples was verified by measuring spring water sample 9 every 2-3 days to observe if the decrease in counts obtained experimentally correspond to the decrease expected for ^{222}Rn. Figure 4 shows both the theoretical (half-life of 3.28 days) and experimental curves of ^{222}Rn decay and, therefore, the presence of ^{222}Rn in the water samples was confirmed. This also means that ^{222}Rn production is not at equilibrium and uranium and its descendants do not support ^{222}Rn production.

Uranium series nuclides are expected to be in equilibrium with ^{222}Rn in closed bedrock systems. However, in groundwater systems, significant dis-equilibria are observed, thus indicating that, in open systems, potential rock interactions can induce significant isotopic fractionations. This isotopic fractionation is related to the α isotopic mineral phase. Emitted α-particles transmit to the daughter nuclide (^{234}Th) kinetic energy which makes it to be ejected from the mineral grain into porewater. The insoluble ^{234}Th will rapidly be adsorbed on the grain surface and in turn will decay into ^{234}U with a half-life of 24.1 days. Being resident on lattice damages and grain surface, ^{234}U will be transferred as soluble form into the water phase (Kigoshi, 1971; Osmond and Cowart, 1976). Weathering of rocks increases the exposed surface increasing the solution of ^{234}U compared to immobile ^{238}U creating strong isotopic fractionations.

Under closed system conditions, such as in rocks, ^{238}U-series radionuclides should come to secular radio-equilibrium due to radioactive decay after 1.25 Ma such that their ^{234}/^{238}U ratio would be ~1 within the bulk of the rock matrix (Elliot et al., 2014). The activity ratio of ^{234}U/^{238}U found varies between 0.9 and 2.8, so open system condition in some of the samples was observed.

Taking into account all of these results, it can be concluded that, in our study, the presence of ^{222}Rn in spring water samples at higher activities than its parent radionuclides (^{238}U, ^{234}U and ^{226}Ra). This can be due to the fact that ^{222}Rn has high solubility in water and high mobility due to its gaseous nature so it can migrate from the earth's crust containing ^{226}Ra and ^{238}U to spring

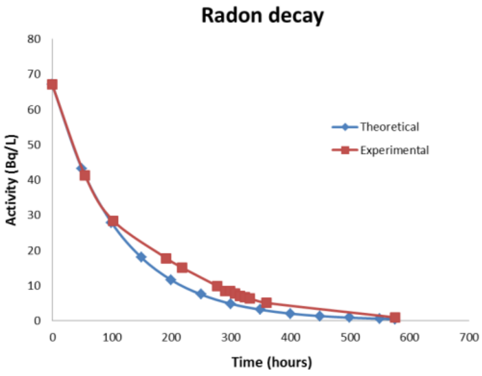

Fig. 4. Theoretical and experimental curve of radon decay obtained for the spring water sample number 9.

waters and the air. However, it should be pointed out that apart of this parameter, there are numerous factors which influence the mobility of the different nuclides in water.

3.4. Ingestion doses from spring water consumption

Radiological effects owing to the ingestion of dissolved ^{222}Rn in drinking water are defined in terms of the effective radiation dose received by the population through the habitual consumption of water. As such, the annual effective dose due to spring water ingestion for adults was calculated as stipulated by UNSCEAR (UNSCEAR, 2008) and is shown in Table 4. The World Health Organization (WHO) and EU directives recommend or stipulate, respectively, a reference level of the annual effective dose received from drinking water consumption of 100 µSv/y. This value excludes the dose received from ^{3}H, ^{40}K, ^{222}Rn and ^{222}Rn decay products. According to the WHO (Organization, 2004), if the dose is lower than 100 µSv/y, the water is suitable for drinking purposes and no additional action is required. In contrast, if the dose exceeds 100 µSv/y, remedial measures to reduce it are suggested. In this study, annual effective doses for all of the radionuclides analysed were calculated. ^{222}Rn was the highest contributor to total annual effective dose for spring water and it ranged between 10 and 765 µSv/y. However, this radionuclide should not taken into account for the annual effective dose in accordance with WHO recommendations and the EU directive, so the total annual effective doses for spring water consumption calculated based on the activities of ^{226}Ra, ^{234}U and ^{238}U varied between 0.8 and 21.2 µSv/y. As a result of this study, the ^{222}Rn concentration of one sample from a granitic region has been found to exceed the level stipulated by the EU Directive, with a value of 104.9 Bq/L. Furthermore, it can be estimated from the concentration of

Table 4. Estimates of annual effective doses (mSv/y) due to ingestion of ^{234}U ^{238}U. ^{226}Ra. ^{222}Rn in spring waters.

Sample number	Effective dose (µSv/y)				
	^{222}Rn	^{226}Ra	^{234}U	^{238}U	Total ingestion*
1●	154.8	1.2	0.9	0.4	2.5
2●	72.3	1.8	0.8	0.4	3.0
3●	81.0	0.6	0.1	0.1	0.9
4●	29.9	0.4	0.4	0.2	0.9
5●	27.0	0.4	0.3	0.2	0.9
6●	54.8	18.6	2.0	0.7	21.2
7▪	24.8	2.0	1.1	0.6	3.8
8◊	765.8	3.9	1.0	0.7	5.6
9◊	651.9	1.2	0.7	0.7	2.6
10◊	233.6	3.3	0.8	0.6	4.7
11†	27.0	1.4	0.3	0.3	1.9
12†	51.1	2.9	0.8	0.5	4.1
13†	10.2	0.6	0.1	0.1	0.9
14●	22.6	0.6	0.2	0.0	0.8
15●	19.7	0.8	0.5	0.2	1.5

* ^{222}Rn excluded

●	Limestones, marlstones, sandstones, dolomite.
▪	Conglomerates with clay matrix.
◊	Alkaline granites and granodiorites.
†	Siliceous sandstones and clays.

^{222}Rn parents that the doses of radiation exposure from all of the spring water samples were <21.2µSv/y.

4. Conclusions

^{222}Rn activity levels were measured in fifteen spring waters from different geologic areas around Catalonia (Spain) and the results ranged between 1.4 and 104.9 Bq/L. However, the activities of their parent isotopes from the same decay chain varied between 2-91 mBq/L, 4-55 mBq/L and <0.2-21.6 mBq/L for ^{226}Ra, ^{234}U and ^{238}U respectively. The difference of radionuclides activity showed that ^{222}Rn in granitic spring water samples does not originate from ^{226}Ra present in water sample but from the spring rocks, containing ^{226}Ra and ^{238}U, that the water flows through. A relationship can be observed between ^{222}Rn concentration and the geological composition of the spring. High values of ^{222}Rn concentration were found in granitic regions, as expected, and near geologic faults. Comparing the measured ^{222}Rn concentrations in spring water with the reference level of 100Bq/L, it can be concluded that the waters from the public springs analysed in this study did not present elevated concentrations of ^{222}Rn, with the exception of sample number 8.

Lastly, the total annual effective dose in spring waters due to ^{226}Ra and ^{234}U and ^{238}U was calculated for all of these samples and annual effective doses lower than the stipulated level (100 µS/y) were obtained. Therefore, all of the spring water samples analysed comply with the requirements for radionuclide content in drinking water and are suitable for consumption from a radiological point of view.

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Annex II. Llistat de publicacions sorgides arran d'aquesta Tesi Doctoral.

Les següents publicacions estan incloses en la part experimental, les quals estan publicades, enviades o pendents de publicació en revistes científiques:

E. Fonollosa, A.Nieto, A. Peñalver, F. Borrull, C. Aguilar, Determination of artificial beta-emitters in sludge samples, J. Radioanal. Nucl. Chem. (accepted).

E. Fonollosa, A. Peñalver, C. Aguilar, F. Borrull, Polonium-210 levels in different environmental samples, Environ. Sci. Pollut. Res. 22 (2015) 20032–20040.

E. Fonollosa, A. Peñalver, C. Aguilar, F. Borrull, Bioaccumulation of natural radionuclides in molluscs from Ebro Delta area, Environ. Sci. Pollut. Res. (submitted)

E. Fonollosa, A. Peñalver, F. Borrull, C. Aguilar, Radon in spring waters in the south of Catalonia, J. Environ. Radioact. 151 (2016) 275–281.

A més d'aquestes publicacions, també s'ha publicat un "review" i un altre article per a una revista de divulgació:

E. Fonollosa, A. Peñalver, C. Aguilar, F. Borrull, A. Colom, J. Ruana, Caracterización radiológica de las aguas de consumo humano en un afluente del río Ebro, el río Martín, Tecnoaqua. 13 (2015) 34–40.

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